THE SIGNIFICANCE OF INDOOR:OUTDOOR RELATIONSHIPS, AND PHYSICAL AND CHEMICAL COMPOSITION IN PERSONAL EXPOSURE TO URBAN PARTICULATE MATTER

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Date.....11/7/2003.....

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Abstract

Over recent years there has been mounting evidence suggesting that airborne particulate matter may be responsible for the aggravation of a number of respiratory illnesses. Because of these health implications it is considered important to understand the sources of airborne particles, the pathways leading to human exposure and the variables affecting the degree of exposure.

The main objectives of this research is to assess the relationships between indoor and outdoor respirable particulate matter, the primary factors influencing this relationship and how this may relate to personal exposure. In addition, it was also felt important to determine any relationships between different sources and sinks of particulate matter, such as street dust and dust present on indoor surfaces.

Simultaneous indoor and outdoor measurements of respirable particulate matter were undertaken in three buildings located in Wolverhampton City Centre. Two of the buildings are situated in a road used by approximately 10,000 diesel buses each day, with 4 and 5 storey buildings along both sides of the road producing a small street canyon effect. Monitoring indoor and outdoor particulate concentrations inside one of these buildings for one year has shown that meteorology, building location and building use can have a significant effect upon airborne particulate concentrations both indoors and outdoors. For example, a greater wind speed caused an increase in particles penetrating indoors and particulate levels were generally lower, indoors and outdoors, when wind was flowing parallel to the canyon. Particulate concentrations were also

significantly greater inside the street canyon and the buildings located within the canyon when compared to another location in Wolverhampton City Centre. Chemical analysis of airborne particles and deposited dusts suggests that the majority of the particulate in the busy street canyon is likely to be diesel engine and vehicle related. The magnetic signature of the dusts collected from the street canyon also varies from dusts collected from other locations, for example the χARM/SIRM ratio is approximately half of other street dusts collected in the West Midlands.

Airborne particulate, street dusts and surface dusts from several roads and buildings were chemically and morphologically analysed using a variety of methods to assess the relationships between these sources and sinks of particulate matter. This analysis suggests that dust moves freely between being airborne or deposited, enabling the formulation of a schematic model, illustrating this movement.

Contents

Chapter 1

Introduction

This thesis describes research conducted at the University of Wolverhampton, involving particulate air pollution. This pollutant is more properly termed airborne particulate matter and is also variously referred to as aerosol and suspended dust. The motivation behind this research has been to improve understanding of the nature of urban particulate matter and specifically how this relates to indoor air quality and personal exposure.

The UK Department of the Environment, Food and Rural Affairs (DEFRA) currently monitors airborne particulate matter as PM_{10} at central monitoring stations throughout the UK. However, because most people spend the majority of their time indoors (Szalai, 1972; Richardson *et al.,* 2001), the levels recorded at these sites are often not considered to be representative of the levels to which people are exposed. This may be especially true inside buildings located within street canyons where the particulate concentrations can be far greater than background levels. Therefore, an understanding of the indoor:outdoor relationships of particulate matter is important in estimating personal exposure.

This research focuses on the measurement of airborne particles in the respirable size fraction (50% cut-off at 4 μm according to the International Standards Association). This size classification was chosen as this size of particle can penetrate to the un-ciliated

airways of the lung (alveolar region). Therefore, particles of this size and smaller may be responsible for aggravating diseases of the deep lung, such as pneumoconiosis, whilst PM_{10} may be relevant to incidences of bronchitis, asthma and other upper airway diseases.

Dust can exist as either airborne particles or dust that has settled on to floors or other surfaces. Previous studies have suggested that settled dust can be considered as both a sink (through deposition) and a source (through re-suspension) of airborne particulate matter. The precise relationships, which exist between these two phases of dust, are currently uncertain. This research attempts to clarify this relationship by examining the chemical and physical relationships between settled dust and airborne particulate matter.

University of Wolverhampton buildings, located in Wolverhampton City Centre, were used for the majority of the measurements of both settled dusts and airborne particulate matter, undertaken during this investigation. Wolverhampton is an industrial city with a population of approximately 250,000 and is located around 25 km north west of central Birmingham in the West Midlands conurbation (population approximately 2.55 million).

Chapter 2

Literature Review

2.1 Introduction

Airborne particulate matter consists of a complex mixture of suspended solid and liquid and is often collectively termed an aerosol (QUARG, 1993). There is a wide variation in both the physical and chemical properties of airborne particles. Particles, originating from natural sources, such as sea spray and wind blown soil, tend to be relatively coarse in comparison to particles, arising from anthropogenic sources, such as vehicle emissions. Fine particles can be transported long distances in the atmosphere and can penetrate deeply into the lungs, whereas coarse particles are normally deposited in the upper airways. The International Standards Association (ISO) has categorised particles by size, depending upon their ability to penetrate into the human respiratory system (QUARG, 1996) (Figure 2.1).

'Inhalable' particles are defined as those particles which can enter the nose and mouth and include particles up to 100 μm in diameter. 'Thoracic' particles are those which can penetrate beyond the larynx. The ISO definition of thoracic particles are those which have a 50% cut-off at 10 μm and corresponds to the widely used PM_{10} classification. The 'respirable' convention includes those particles which penetrate to the alveolar region of the lungs and has a median cut off at 4 μm. There is also an ISO definition of a 'high risk' respirable fraction which represents the respirable fraction for children and

adults with illness. This has a median cut-off at 2.5 μm, corresponding to the $PM_{2.5}$ classification.

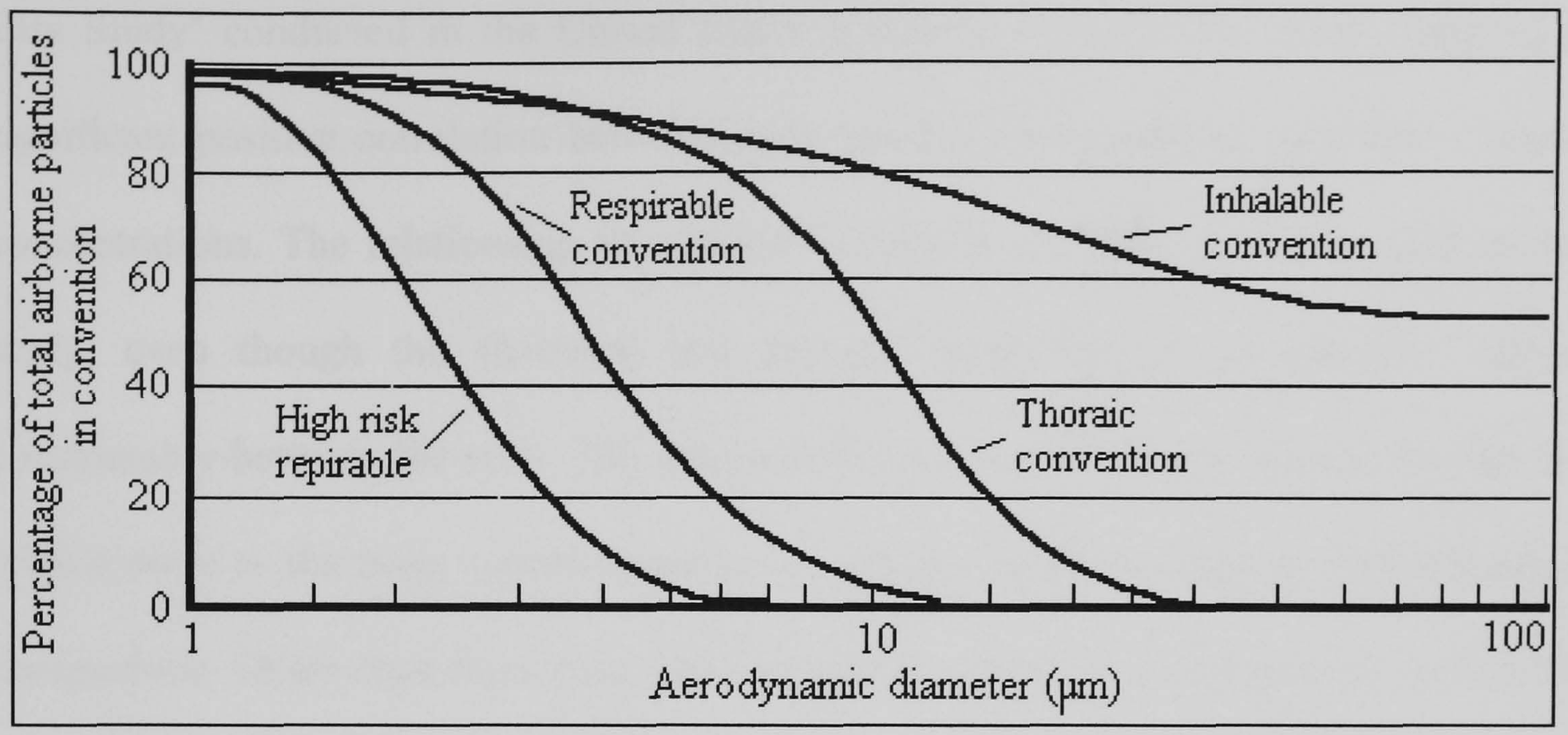


Figure 2.1: ISO health related particle sampling conventions ISO 7708 (1994)

(Source: QUARG, 1996)

2.1.1 Particulate matter and health

Airborne particulate matter is now receiving world-wide attention because of its impact on air quality, in particular, the increasing evidence that airborne particulate matter can be linked with respiratory illness and heart problems (Hruba *et al.,* 2001; Morris, 2001). Epidemiological studies have shown clear relationships between airborne particulate matter, measured gravimetrically and mortality (Dockery, *et al.,* 1993; Pope, *et al.,* 1995). In addition, some studies have shown that it is likely to be the finest particles that have the greatest impact upon health (Schwartz *et al.,* 1996). Therefore, there is now increasing pressure on governments to incorporate $PM_{2.5}$ limits into air quality standards.

Evidence of the health threat posed by airborne particulate was presented in 'The Six City Study' conducted in the United States (Dockery *et al.,* 1993). They observed a significant positive correlation between daily mortality and ambient particulate matter concentrations. The relationship was found to exist in all of the six cities used in the study, even though the chemical and physical properties of the particles varied considerably between the sites. This suggests that the health effects of particles may be related more to the mass concentration and number of particles than to their chemical composition. Death rates from heart and lung disease in the most polluted city were 37% higher than in the least polluted city. A 10 $\mu g\ m^{-3}$ rise in PM_{10} levels was found to be associated with an increase of 1% in mortality rate. This relationship was observed for increases in PM_{10} concentrations at all levels, including those at concentrations well below the United States air quality standard.

Pope *et al,* (1995) conducted a larger study using data from over 500,000 adults and ambient air pollution levels in 151 cities in the United States over an 8 year period. As with the 'Six City Study', fine particles were found to be associated with mortality after the removal of confounding factors such as tobacco smoking.

It appears that the effect that particles have upon health is not related to chemical composition. Where measurements of the chemical composition of particles have been made, it is clear that toxic species are not normally found in concentrations consistently high enough to cause any pathological effects (Department of Health, 1995). Therefore,

there is no universally accepted explanation for the observed relationship between fine particles and adverse human health effects. However, Pope *et al.,* (1995) observed that sulphate particles are significantly associated with cardiopulmonary disease and lung cancer.

One hypothesis suggests that the health effects arise from the body's defensive reaction to ultrafine particles diffusing onto the surface of the lungs (Seaton *et al.,* 1995). As the immune system responds to individual particles present in the lungs, it may not be the overall mass concentration but rather the number of particles smaller than 0.1 μm in diameter and possibly their chemical composition, which is the determining factor. They also observed that rats, exposed to biologically inert PTFE and titanium dioxide, only developed adverse health effects when the particle diameter was smaller than 0.1 μm. This finding was further supported by research conducted in Germany (Air Health, 1996).

2.2 Sources of particulate matter

There are a wide variety of sources of particulate matter within urban areas. Indoor sources include tobacco smoking, cooking, heating systems and re-suspension of settled dusts. However, in buildings without a significant indoor source, the majority of particles found indoors can be assumed to originate from outside. Outdoor sources are more varied and can be basically divided into natural and anthropogenic sources. Natural sources tend to include wind blown soil, sea spray and plant pollens and spores.

Anthropogenic sources are highly varied and include motor vehicle emissions, road dust re-suspension and industrial emissions. Generally, within urban centres anthropogenic emissions are more numerous than natural sources and add a greater quantity of particulate matter to the overall dust burden of the atmosphere.

The structure of buildings within urban areas can also increase the relative importance of certain sources. For example, street canyons can restrict the dispersion of traffic related particulates, causing locally high concentrations (Namdeo *et al.,* 1998; Huang *et al.,* 2000).

2.2.1 Natural sources

The action of wind blowing over loose and dry soil leads to the suspension of particles into the air. This source of particulate matter is mainly associated with arid, sandy and sparsely vegetated areas. Therefore, it may be assumed that in a relatively wet climate, such as the UK, this source of particulate matter does not add significantly to the total dust burden of the urban atmosphere for the majority of the year. The diameter of these mechanically generated particles is typically between 1-10 μm (Murphy, 1984). The relatively large diameter of these particles, relative to the majority of particulate matter, means that deposition occurs quickly and their residence time in the atmosphere is short. However, once deposited dust can become re-suspended again under dry, windy conditions (Twomey, 1977; QUARG, 1996).

Because the UK is surrounded by sea, the contribution of sea salt to the atmospheric aerosol load in the UK is significant (QUARG, 1996). The action of waves and wind generates spray, which as the water evaporates leaves salt suspended in the atmosphere. The crystalline nature of salt means that aerosols formed by this process tend to be relatively coarse in size, with particles normally being in the 0.5-10 μm diameter range (Murphy, 1984). Inland urban areas such as Wolverhampton may not be affected by this process to the same degree as more coastal UK cities and towns (Harrison and Jones, 1995). In the winter, rock salt is applied to urban roads as a de-icing agent. Suspension of this salt by wind and traffic is known to add to the salt burden of the atmosphere in urban areas (Willison *et al.*, 1989).

The third major natural source of airborne particulate matter is biological particles, such as spores, pollen, bacteria, viruses and natural fibres. Although controlled by the same physical processes as anthropogenic particles, they are mainly of concern in terms of allergenic responses and biological activity (COMEAP, 1995; QUARG, 1996).

2.2.2 Diesel exhaust particulate and vehicle emissions

In urban centres exhaust emissions from automobiles are thought to be the dominant source of PM_{10}, although nationally other sources are of greater importance (Figure 2.2).

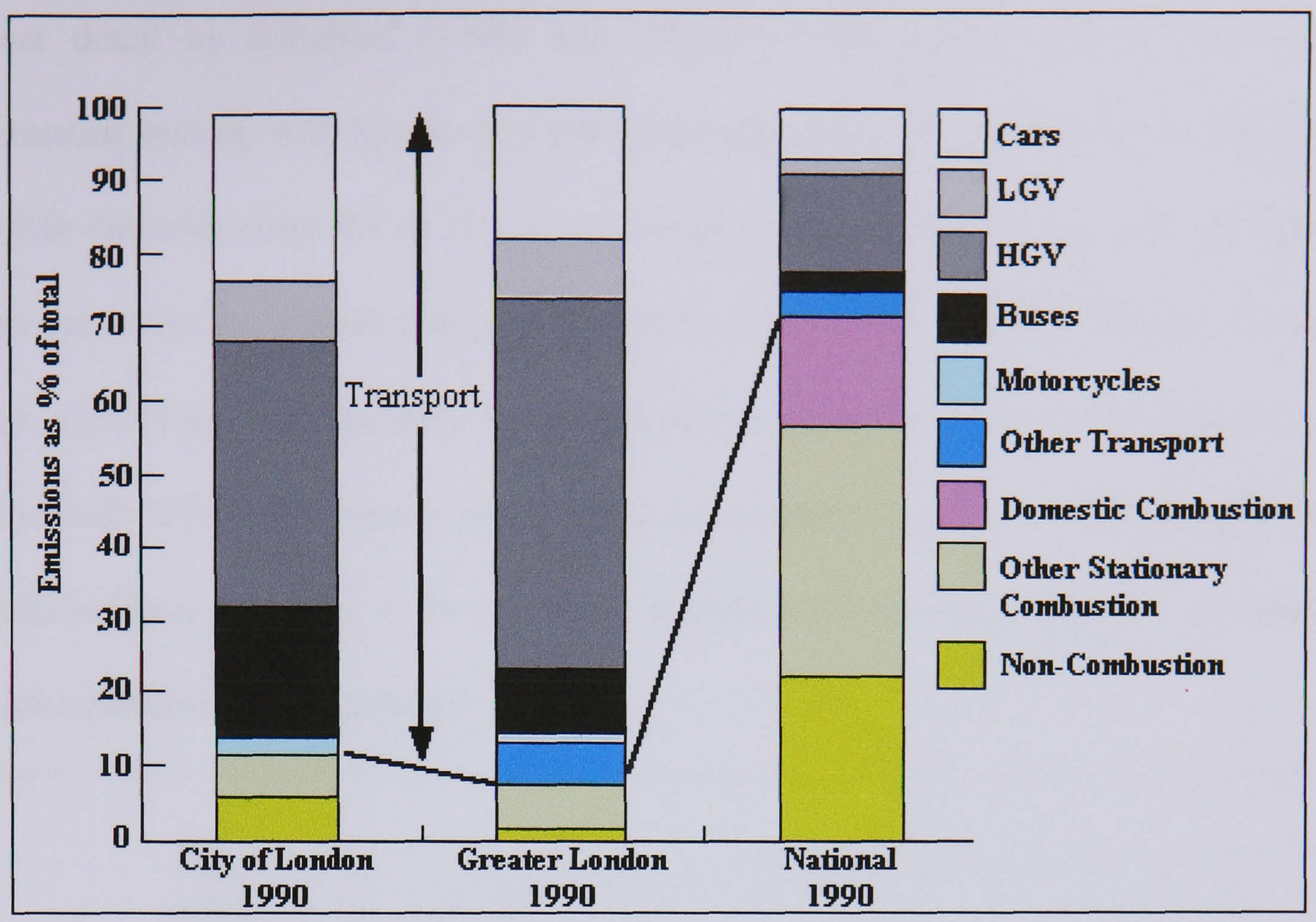


Figure 2.2: Percentage of particulate emissions of PM_{10} from different sources

(Source: Adapted from QUARG, 1996)

Diesel fuel combustion has also been identified as the single most significant contributor of fine particulate material to urban areas; estimated at 20% in 1993 (COMEAP, 1995; Berube *et al.,* 1997). It has also been shown that indoor levels of particulate matter are heavily influenced by traffic from outdoors (Thompson *et al.*, 1973). Diesel engines are of particular significance as they emit particulates at a far greater rate than petrol or spark ignition engines, with typical emissions being 10 to 100 times greater than comparable petrol engines (Sagai and Ichinose, 1994; Kittelson, 1998). In addition, several studies show that almost 100% of diesel particles are smaller than 10 μm in diameter (USEPA, 1995; Kleeman *et al.,* 2000) (Figure 2.3). The mass and number distribution of particles emitted by diesel engines has been examined in

closer detail by Kittelson (1998) and Berube *et al.,* (1999). These studies gave contrasting results, with Kittelson (1998) observing that the majority of mass was in the particle diameter range 0.1 to 10 μm, whilst approximately 90% of particles by number were present in the diameter range 0.005 μm to 0.05 μm (Figure 2.4). However, Berube *et al.,* (1999) reported that only 10% of particles by number were smaller than 0.1 μm, with nearly 90% being present in the 1 to 2 μm diameter range. The differences in these results is likely to be due to the collection method used and the preparation of samples, as acknowledged by the authors.

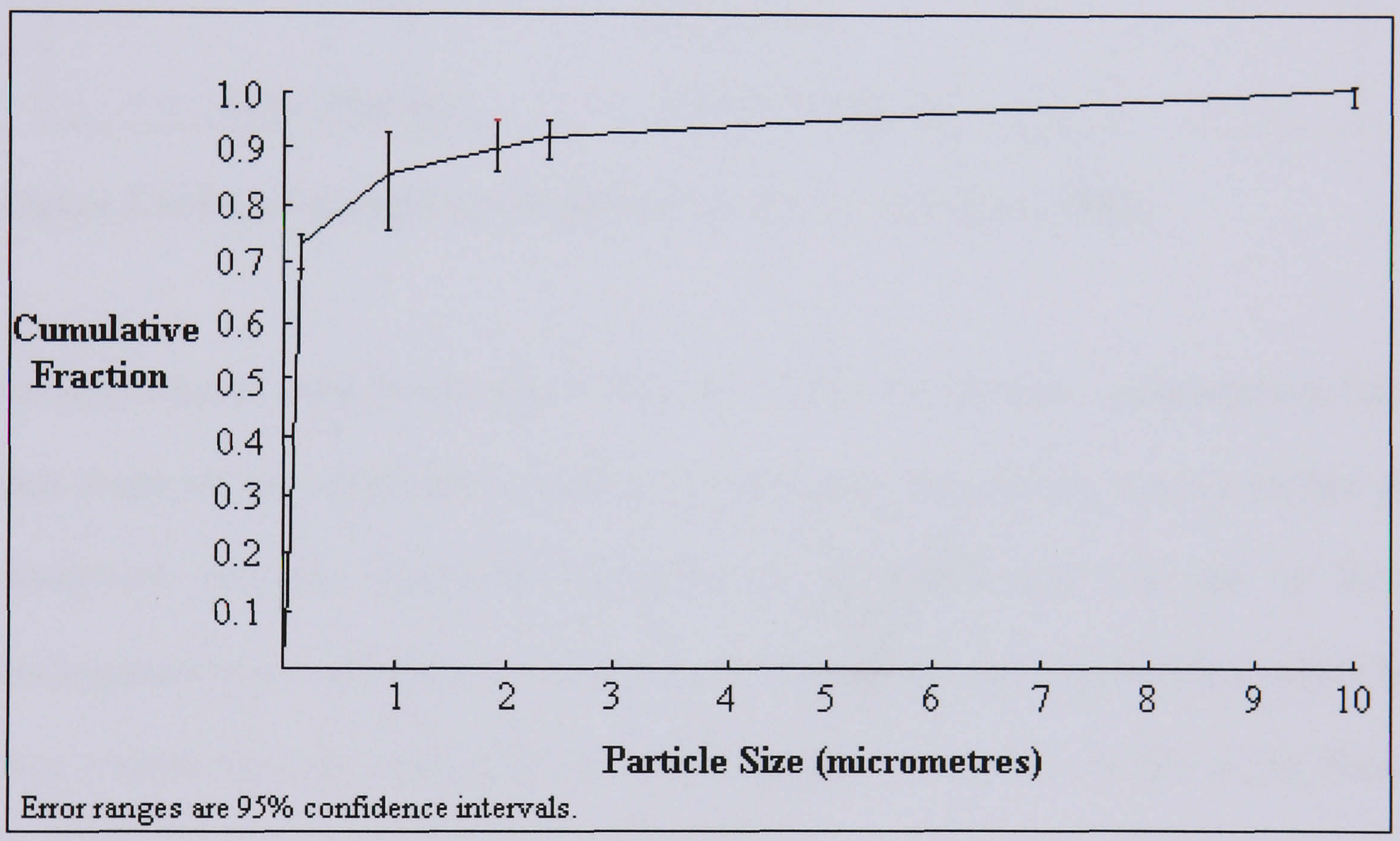


Figure 2.3: Size distribution of particulate emissions from diesel engine cars (Source: USEPA, 1995)

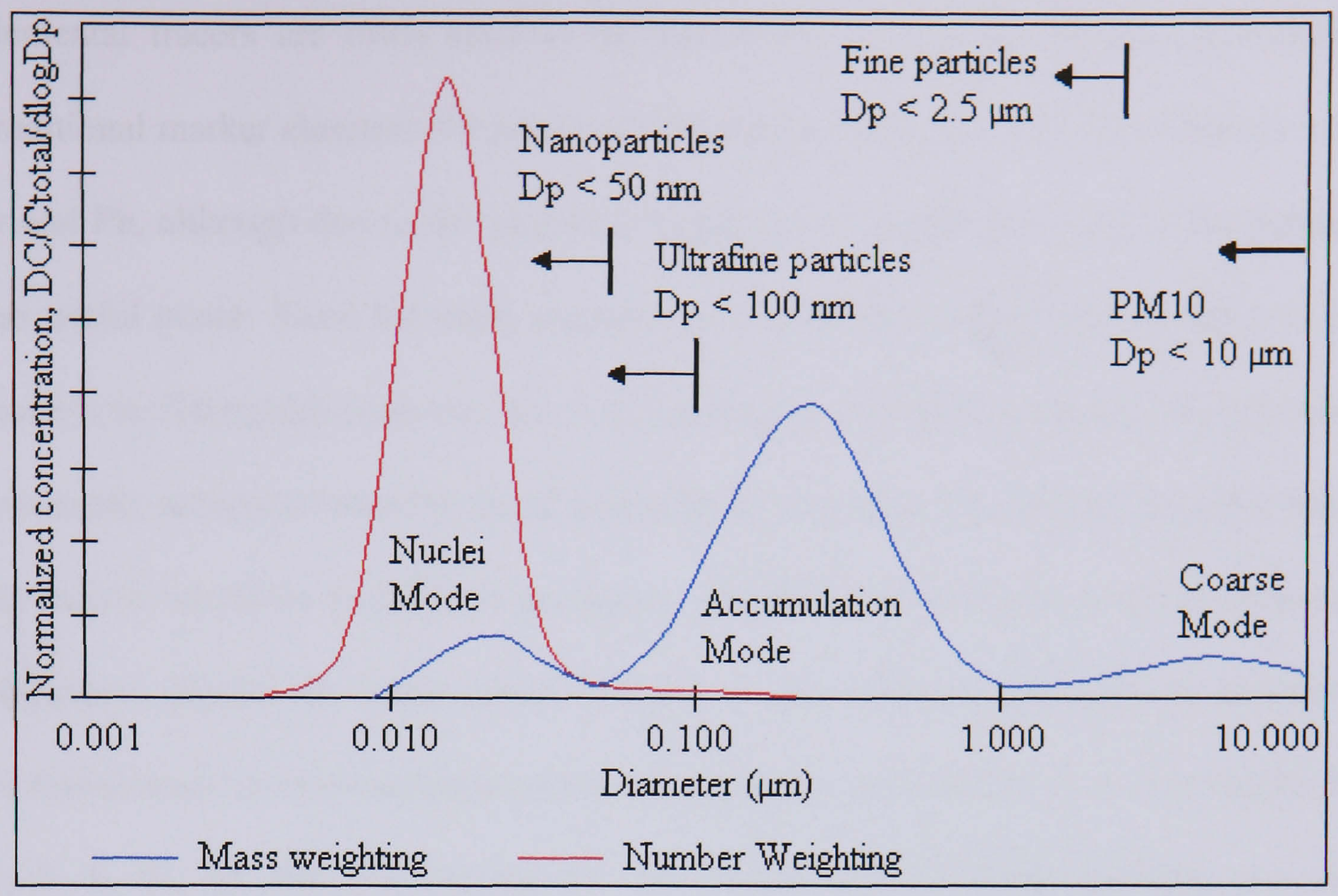


Figure 2.4: Diesel particle size distribution (Source: Kittelson, 1998)

In diesel engines solid particles are formed as a result of incomplete combustion in fuel rich zones of the combustion chamber. During diesel combustion a spray of fuel is introduced into the combustion chamber. Upon compression the fuel is then incompletely burnt to leave a very fine aerosol of pyrolysed and unburned fuel, which is then emitted from the exhaust (Barnard and Bradley, 1985). This results in the black soot characteristic of diesel exhaust emissions.

Three main factors have been highlighted which affect both the physical and chemical characteristics of diesel generated particulate matter (Bartlett *et al.,* 1992):

1. Chemical composition of fuel and lubricating oil.
2. Engine operating conditions.
3. Engine design and condition.

Elemental tracers are often used to determine the sources of airborne particulates. Traditional marker elements for particles originating from petrol powered vehicles were Br and Pb, although due to the gradual phasing out of leaded petrol, Pb is becoming a less useful tracer. Since the main constituent of diesel particles is carbon and it is not possible to distinguish between carbon originating from different sources, an equivalent universally accepted tracer for diesel particulates is as yet undiscovered. If such a tracer did exist it would be possible to accurately determine the quantity of diesel generated particulate present in urban areas. Berube *et al.,* (1999) conducted an extensive elemental analysis of diesel particulates and found the presence of C, O, Na, Mg, K, Al, Si, P, S, Cl, Ti, Mn, Fe, Zn and Cr. The morphology of diesel particles was also investigated and four main morphological categories were identified and termed spherulites, chains/clusters, spherules and flakes (Figure 2.5).

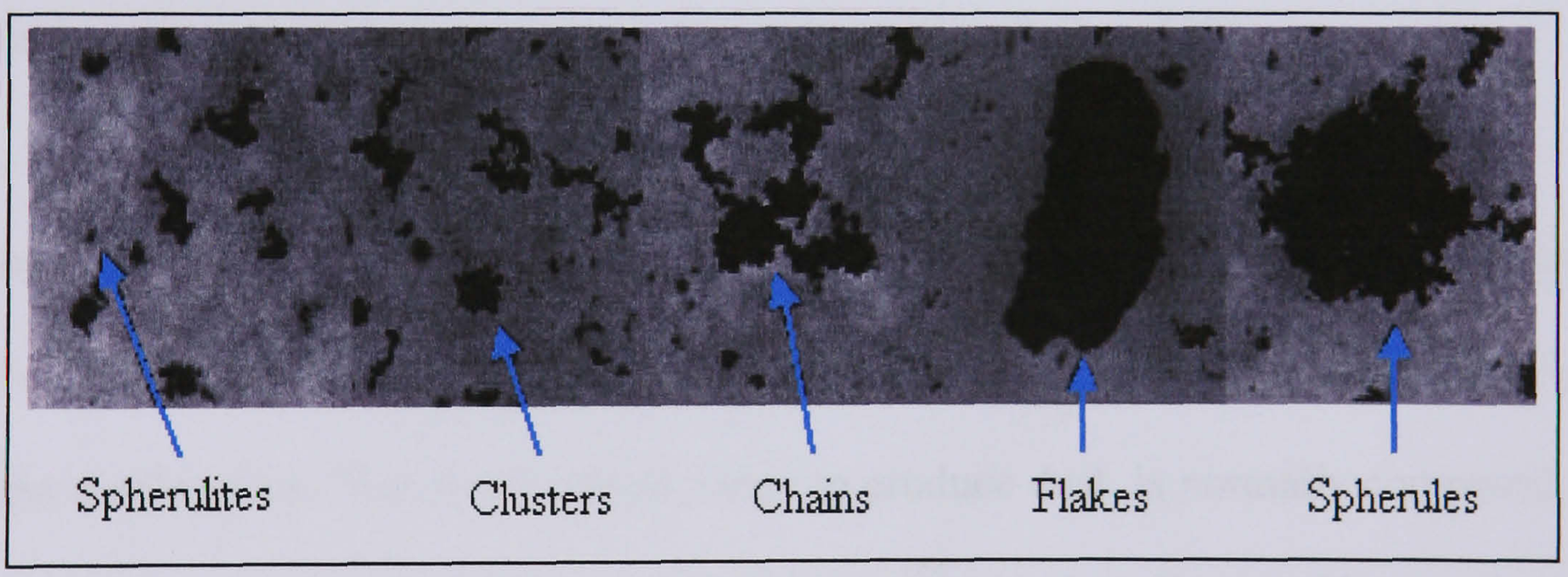


Figure 2.5: Electron micrograph of diesel particle morphologies (Source: Berube *et al.*, 1999)

Diesel particles are also considered a potential human health hazard, mainly because of their small diameter, but also because of the presence of polycyclic aromatic

hydrocarbons (PAH) in the solvent organic fraction of the particulates (Williams *et al.*, 1989). Some of these PAHs are known human carcinogens. These PAHs can be adsorbed on to the surface of diesel particles and because the particles are deposited deep into the lung, they act as a vehicle for transport for these compounds. The carcinogenic properties of diesel emissions have been highlighted in many studies, where rats have been exposed to diesel particles (Pott and Roller, 1997; Iwai *et al.*, 1997). These studies indicate that they can cause lung cancer in laboratory rats when exposed to very high concentrations for prolonged periods of time, for example, Iwai *et al.,* (1997) found that the incidence of tumours in rats exposed to diesel particulates increased with increasing particulate dose. However, the quantities of diesel particulate to which the rats are exposed in such studies are often very high, being far greater than levels to which humans are likely to encounter. Thus, it is widely considered unreasonable to extrapolate results from these toxicological studies across to the typical ambient concentrations encountered by humans (McClellan, 1996).

In addition to engine emissions, automobiles also produce particulates through tyre and brake wear. Particles are produced mechanically due to the rolling shear of the tyre on the road surface. Tyre tread, which wears to produce dust, is normally composed of co-polymers of natural rubbers, polyisoprene rubber, butadiene rubber and styrene-butadiene rubber. The precise composition of the tyre is obviously one of the main determinants in the chemical composition of the particulates produced. The type of rubber or the blend of rubbers used in the manufacture of the tyre is dependent upon factors such as the physical strength and wear resistance required by the vehicle. The

quantity of particulate generated is highly dependent upon several factors including driving conditions (acceleration, average speed, braking *etc.*), tyre conditions (pressure, age of tyres, *etc.*) and the type of road surface (asphalt or concrete). Several authors have attempted to quantify the amount of particulates generated by tyre wear, for example, The United States Environmental Protection Agency (USEPA, 1995) gives values for PM_{10} emissions from car tyres as 0.0012 g km^{-1} whilst values as high as 0.09 g km^{-1} have been reported elsewhere (Wolfgang *et al.,* 1993). In general, it is thought that particulates produced by tyre wear are unlikely to be smaller in diameter than 2.5 μm due to the physical nature of the mechanisms leading to their generation (QUARG, 1996).

Brake lining dust is produced under forced deceleration due to the wear of the brake disk. Because brake manufacturers use many different materials for the manufacture of brake linings, the dust may contain a variety of contaminants. The USEPA (1995) has also attempted to quantify emissions from brake linings and has suggested a value for cars of 7.95 X 10^{-3} g km^{-1}. Because these values suggested by the USEPA are for cars alone, these figures would need to be proportionally increased to take into account the larger tyres and brakes of buses and heavy goods vehicles. Tyre and brake wear is a far less important source of PM_{10} from automobiles than engine emissions (USEPA, 1995) (Table 2.1). For example, a car travelling in normal urban conditions with a 1.7 litre diesel engine will emit between 0.17 and 0.34 g km^{-1} of PM_{10} under hot and cold running conditions, respectively. For the average diesel powered bus the emissions factor is far greater, being in the range of 1.6 g km^{-1} of PM_{10} (USEPA, 1995)

Table 2.1: Emissions of PM_{10} from automobiles (Source: USEPA, 1995)

Source of Emission	PM_{10} Emitted ($g\ km^{-1}$)
Tyre Wear (Petrol car)	1.2×10^{-3}
Brake Wear (Petrol car)	7.95×10^{-3}
Exhaust Emission (Diesel car)	0.17-0.34
Diesel Bus Exhaust	1.6

2.2.3 Re-suspension of street dust by motor vehicles

Dust deposited on the road surface can be re-suspended into the atmosphere by the movement of vehicles along the road (USEPA, 1995; QUARG, 1996). This dust may originate from deposited atmospheric dust, material carried on to the road surface by vehicles and erosion or wear of the road surface. There is no known chemical tracer, allowing this source to be discriminated from other sources, such as wind blown soil or dust from demolition sources. However, work at the University of Birmingham, England quantifies this component through its calcium or iron content (Harrison, 2001). The United States Environmental Protection Agency have attempted to include re-suspended road dusts in their emissions inventories, but the results are, generally, regarded with low credibility. The data used to derive these emission estimates was based on the dry climate of the USA meaning that extrapolation to the wetter climate of the UK can be difficult (QUARG, 1996). The particulate emission factor for paved (USEPA, 1993) and unpaved roads (USEPA, 1988) is calculated from the following equations:

$$\text{Unpaved} = \frac{453.592 \times 5.9 \times \text{PSDUNP}\ (\text{UNSLIT}/12)\ (\text{SPD}/30)}{(\text{VWEIGHT}/3)^{0.7}\ (\text{WHEEL}/4)^{0.5}\ (365\text{-IPDAYS}/365)} \qquad \text{Eqn. (2.1)}$$

$$\text{PAVED} = \text{PSDPVD}\ (\text{PVSSILT}/2)^{0.65}\ (\text{WEIGHT}/3)^{1.5} \qquad \text{Eqn. (2.2)}$$

Where:

UNPVD = The fleet average road dust emission factor.

PSDUNP = The fraction of particles less than or equal to the particle size cut off.

UNSILT = The percent silt content of the surface material.

SPD = The average vehicle speed (mph).

WEIGHT = The fleet average vehicle weight (tons).

VWHEEL = The fleet average of wheels.

IPDAYS = The average number of precipitation days per year with greater than 0.01 inch of rain.

453.592 = The number of grams in one pound.

PAVED = The fleet average paved road dust emission factor ($g\ mi^{-1}$)

PSDPVD = The base emission factor for the particle size cut-off.

PVSILT = The road surface silt loading ($g\ m^{-2}$)

One of the main factors determining the emission factor is the silt loading of the road. In this equation silt is defined as material less than 75 μm. The silt loading of the road is the mass of silt in a square metre of road surface.

The empirical model for unpaved roads was developed from a broad database (Fitzpatrick, 1987) and agrees well with field results (Muleski and Stevens, 1992;

Claiborn *et al.,* 1995). However, for paved roads, the algorithms were based on the results of a limited number of emission tests. Zimmer *et al.,* (1992) concluded that it may not be representative of all urban paved road conditions. They suggested that the paved road equation should not be applied to cases where the range of silt loading is outside the range which was used to develop the equation and there is a requirement to improve the emission factor algorithms. Subsequent research has shown that the equation for paved roads tends to over predict the emission factors (Zimmer *et al.,* 1992; Kinsey, 1993; Claiborn *et al.,* 1995; Kantamaneni *et al.,* 1996). Kantamaneni *et al.,* (1996) found an inverse correlation (R^2 = 0.413) between atmospheric relative humidity and emission factors for paved roads. They suggested modifying the equation as follows:

$$\text{Emission factor (g km}^{-1}\text{)} = -0.0225 \text{ relative humidity (\%)} + 1.7724 \qquad \text{Eqn. (2.3)}$$

However, the climate in the UK is generally wetter than the areas of the USA used for this research. Therefore, it is likely that the true annual average emission factor is even lower and further investigation is needed to quantify this source accurately (QUARG, 1996). Thus, for paved roads, the empirical equation can be further modified to incorporate relative humidity. It has been observed that that if relative humidity is zero, then predicted concentrations are very close to measured concentrations and continue decreasing with increasing relative humidity. The modified equation for paved roads is as follows (Singh, 1997):

$$ERPAVED = (PVSILT/2)^{0.65} (WEIGHT/3)^{1.5} \left(\frac{-0.0225RH + 1.7724}{1.7724 \times 1.6} \right) \quad \text{Eqn. (2.4)}$$

Where:

ERPAVED = The Fleet average paved road dust emission factor (g km^{-1}).

PVSILT = The road surface silt loading (g m^{-2})

WEIGHT = The fleet average vehicle weight (tons).

RH = Atmospheric relative humidity.

However, the use of the above equation is limited to a relative humidity of less than 78%. In this equation, for a relative humidity of greater than 78% re-suspension of road dust is assumed to be zero.

2.2.4 Street canyon effects

Because a significant quantity of urban particulates originate from automobile sources, the dispersion of particulates in street canyons is an important factor. The term street canyon refers to a relatively narrow street between tall buildings, which line up continuously along both sides (Nicholson, 1975). This type of road can, therefore, be thought of as having relatively high pollution due to vehicle emissions (Huang *et al.*, 2000). Hence, buildings within a street canyon are likely to contain increased concentrations of vehicle derived pollutants.

In general, many models of pollutant dispersion within street canyons first consider wind flow distribution. The data are then used to determine the pollution concentration distribution. The main assumption of many of these models is that the diffusion and

emissions from vehicles moving along the street is linear, when the street is straight. It is also assumed that the air in the canyon has a varying pressure and a constant density.

The air flow in urban street canyons is mainly controlled by canyon geometry and local meteorological conditions. Street canyon models often consider the canyon in two dimensions, using the canyon aspect ratio (the ratio between building height and street width) when representing the canyon. It is also possible to model the canyon in three dimensions, with such models also taking into account the height:length ratio as well as the height:width ratio of the canyon. However, the majority of published literature only considers the canyon in a two dimensional form.

It is generally accepted that the flow of air and pollutant dispersion in a street canyon is determined by both meteorological conditions and street canyon geometry. With a perpendicular wind direction often producing a vortex, or set of vortices, within the canyon. Therefore, many models use different wind speeds and street canyon geometry to determine pollutant dispersion. The results from these studies agree well with each other and draw similar conclusions.

DePaul and Sheih (1986) observed that the average flow pattern of the vortex cell in a street canyon does not seem to extend beyond roof level and that the velocity vectors at roof level are almost parallel to that of the ambient wind. They concluded that the confinement of the cell within the canyon suggests that the vertical exchange of air between the canyon and ambient atmosphere is limited. However, the vortex motion

contributes to the mixing of pollutants within the canyon. Baik and Kim (1998) also observed that the vortex cell is often completely trapped within the canyon (Figure 2.6).

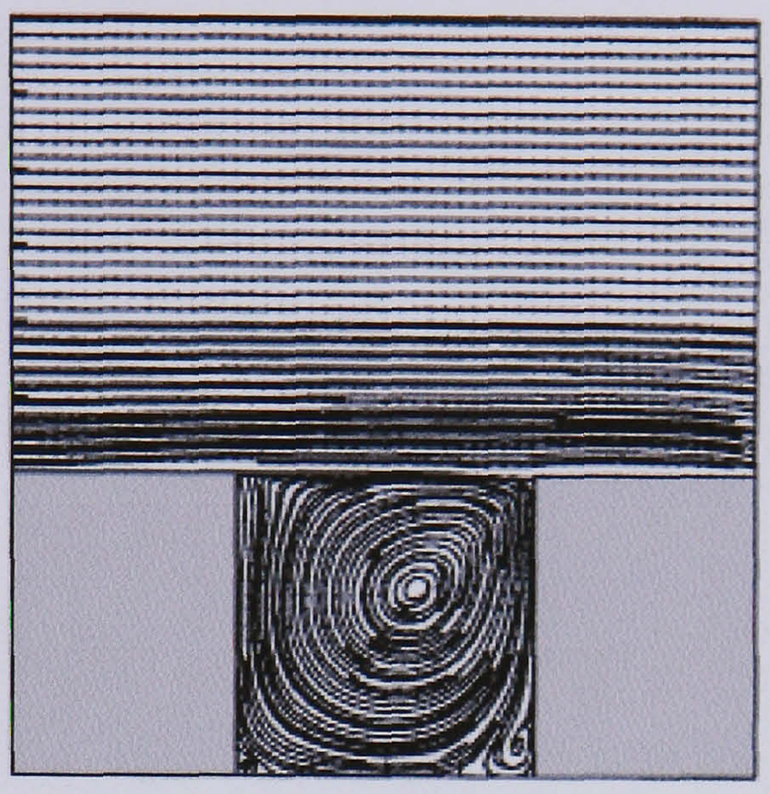


Figure 2.6: Flow field in a street canyon showing vortex almost completely trapped with the canyon (Source: Baik and Kim, 1998)

Huang *et al.,* (2000) formulated a model predicting pollutant dispersion from wind distributions. They found that with a decreasing canyon aspect ratio the centre of the rotating vortex moved closer to the leeward building, and the shape of the vortex changes from being almost circular to elliptical (Figure 2.7).

It was also observed that an increasing wind speed leads to the centre of the vortex moving towards the leeward building, and causes a small vortex to form at the base of the windward building (Figure 2.8). They also found that difference in height between the windward and leeward building was of significant importance to the formation of a vortex. When the leeward building is lower than the windward building, the vortex is seen to move towards the leeward building (Figure 2.9). In contrast, when the leeward

building is higher than the windward building the vortex moves closer to the top of the windward building with an increasing wind speed (Figure 2.10). In the situation they analysed, the vortex disappeared completely when the wind speed was above 1.5 m s^{-1}.

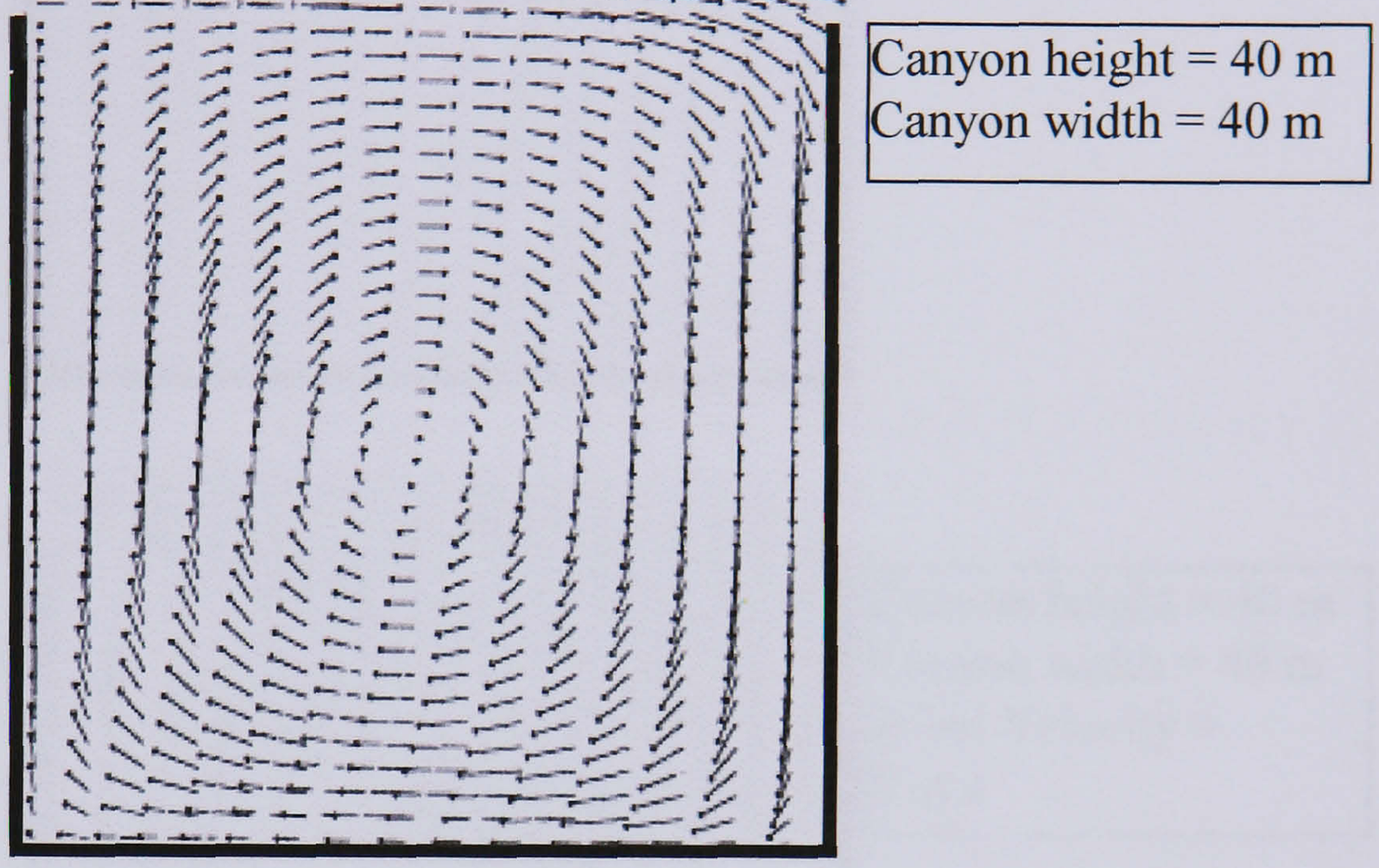
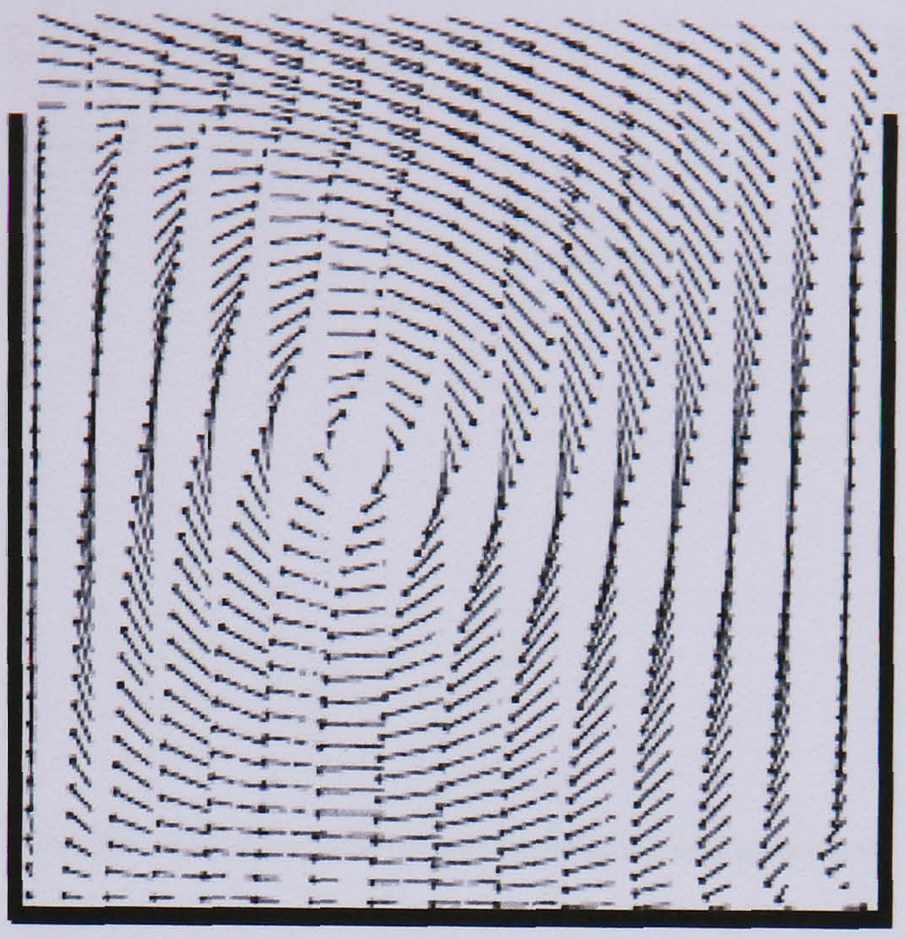


Figure 2.7: Change in vortex characteristic with decreasing canyon aspect ratio (Source: Huang *et al.*, 2000)



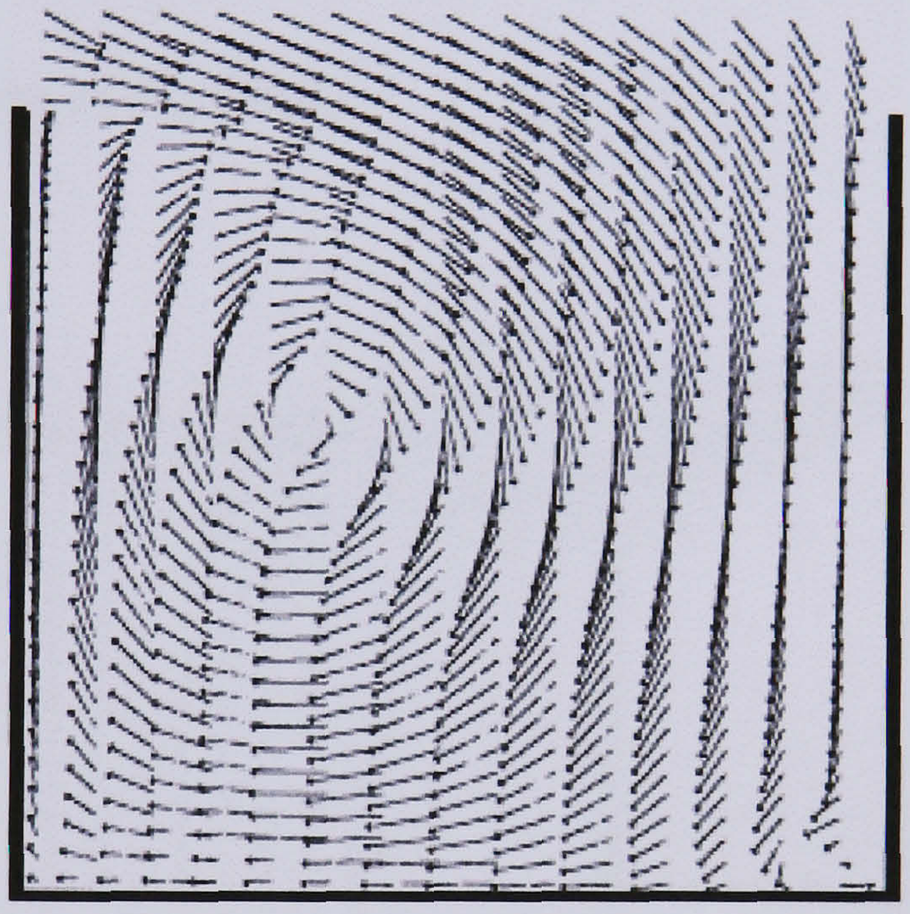


Figure 2.8: Effect of increase in wind speed on the vortex formation in a street canyon (Source: Huang *et al.*, 2000)

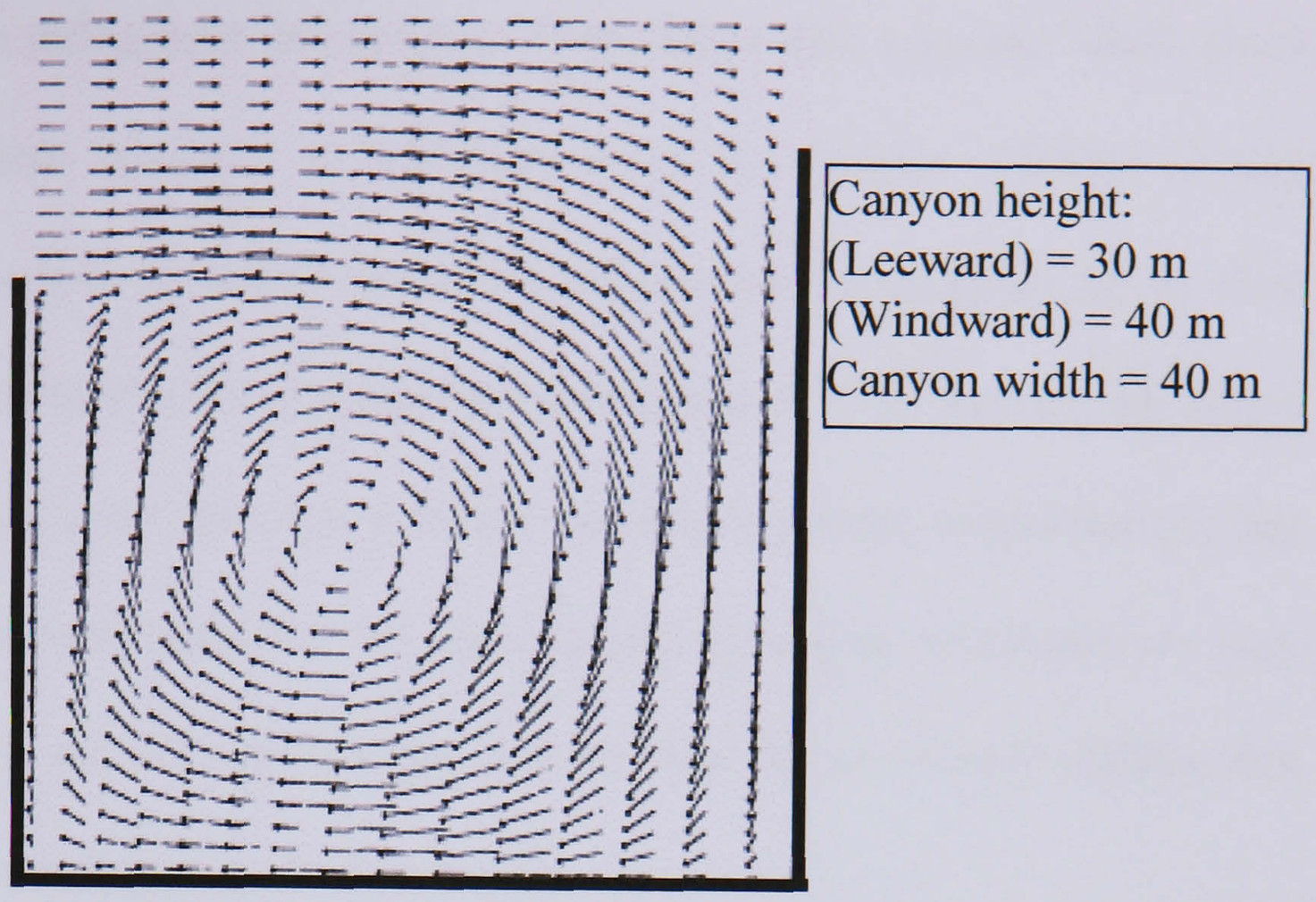


Figure 2.9: Vortex formation when leeward building is lower than windward building (Source: Huang *et al.*, 2000)

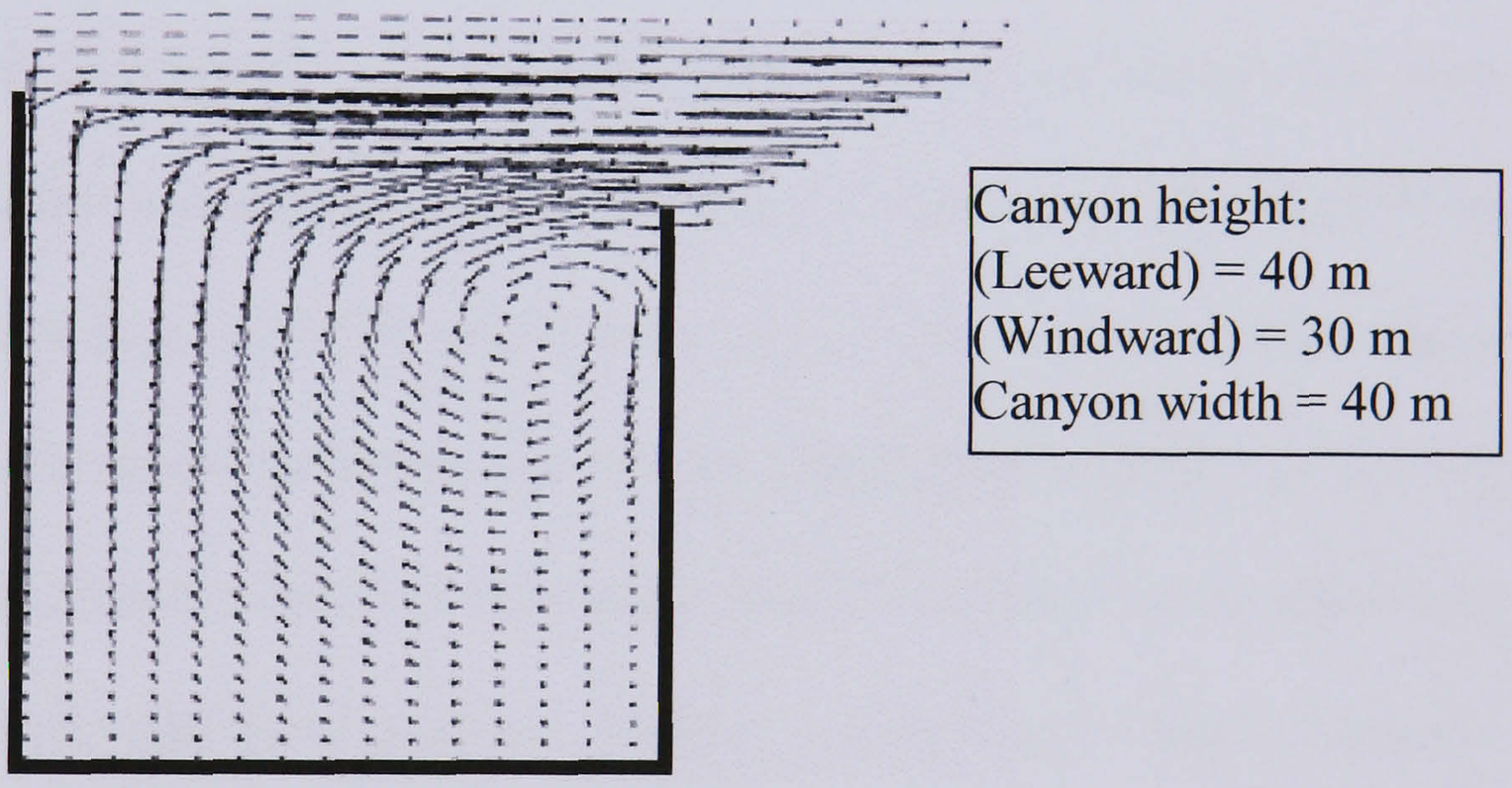


Figure 2.10: Vortex formation when leeward building is taller than windward building (Source: Huang *et al.*, 2000)

They observed that because of this vortex formation, pollutant concentrations can quickly reach a stationary value, and that in general, higher pollutant concentrations exist on the leeward side than the windward side. With increasing wind speed, pollutant

concentrations decrease throughout the canyon. This means that a greater wind speed causes the more efficient removal of pollutants from the canyon. Finally, it was concluded that when the leeward and windward buildings are the same height (in their example, 40 m), it is very difficult for pollutants to be removed from the canyon. When the windward building is taller than the leeward building pollutant concentrations are only slightly lower than when they are the same height. However, pollutants are very efficiently removed when the leeward building is lower than the windward building, due to the vortex moving towards the top of the canyon.

2.3 Indoor:outdoor relationships and particulate matter

It is widely accepted that indoor and ambient particulate concentrations often vary significantly, with indoor concentrations being recorded at anywhere between 45% to 130% of outdoor levels (e.g. Li, 1994 and Colome *et al.,* 1992). This variation has a profound effect upon the actual concentrations of particulate matter to which individuals are exposed. Therefore, it is important to understand the relationships that exist between indoor and outdoor particulate concentrations whenever considering personal exposure. Little is currently known about why this variation occurs. However, local meteorological factors, such as wind speed, humidity and atmospheric pressure may play an important role.

2.3.1 Indoor outdoor relationships and personal exposure

Many people in the UK spend the majority of their time indoors; estimated through activity studies to be around 80-90% of their day (Szalai, 1972; Richardson *et al.*, 2001). Because indoor and outdoor particulate concentrations often vary, ambient particulate concentrations measured at central monitoring stations may not give a true estimation of an individuals pollution exposure. Also, due to the nature and sources of particulates, large variations in concentration can occur over a relatively short distance, for example levels adjacent to busy road intersections may be significantly higher than levels measured at central monitoring stations only several hundred metres away. This implies that fixed monitoring stations can give a poor indication of the exposure of individuals to particulate matter, with data from such stations really only being of use to give a rough estimate of exposure (Sega, 1982). Therefore, in order to accurately quantify an individuals personal exposure to particulates, indoor measurements combined with outdoor measurements are required. It should also be noted that truly quantifying personal exposure can only be achieved through the use of portable exposure monitors, carried with an individual at approximate breathing level.

Personal monitors normally operate on the same principle as static high volume samplers, where air is drawn through a filter at a known rate, causing the filter to capture airborne particles. Pre-exposure and post-exposure weighing of the filter determines the mass of collected particulates. The mass of collected particles and the volume of air sampled is then used to calculate the average concentration of particulate

matter to which the individual has been exposed. However, this equipment has a poor temporal resolution and because the equipment is awkward for the wearer and a diary of activity needs to be recorded for the duration of sampling, finding volunteers for such monitoring can be difficult. It is because of these reasons that strategically placed static monitors are the simplest and often preferred method of estimating exposure.

The main indoor sources of particulate matter are tobacco smoking, fossil fuel heating systems and cooking. However, increasingly in the majority of public buildings in developed countries smoking is prohibited. Also in many commercial office buildings there is little or no cooking performed and the heating systems are normally gas powered with extremely effective flue removal systems. In these types of buildings with few indoor sources, the ingress of particulates from outside and the re-suspension of indoor settled dusts may often be the main source of particulate matter within the building.

Re-suspension of settled dusts from surfaces, especially carpets, can add a significant quantity of suspended particulate matter to indoor air. Carpets can become an important source of indoor dust if the cleaning regime is insufficient in relation to the dust load. The dust present on the carpets may be re-suspended by movement of individuals, hence re-suspension may be a significant indoor particle source. Kivisto and Hakulinen (1981) performed experiments in a controlled chamber with an artificial foot reproducing the activity of walking on a dust covered carpet. It was observed that one of the main determinants of the degree of re-suspension was % relative humidity (RH%), with

maximum re-suspension occurring at a RH of between 70 and 80%. It was also found that particle diameter was of importance, with particles of less than 1 μm in diameter not being significantly re-suspended (assumed to be due to van der Waals attractive forces being more significant for smaller particles). Thatcher and Layton (1995) also found that particles smaller than 1 μm in diameter are not likely to be re-suspended and that activities such as people entering and leaving the room, on average, doubled the suspended particulate concentration. It was concluded that cleaning, especially vacuuming, re-suspended significant concentrations of particles, with the simple movement of people within the room also increasing particulate concentrations.

In buildings (located in close proximity to roads with high traffic levels), with minimal indoor sources it can be assumed that the majority of indoor particulates will likely originate from traffic related sources. Thompson *et al.,* (1973) demonstrated that indoor particulate concentrations were heavily influenced by nearby traffic levels in a building located near to a busy road.

Airborne contaminants can enter a building with ambient air through a number of routes, including open windows and doors (natural ventilation), air conditioning systems (mechanical ventilation) and adventitious leaks. Gaps around windows, doors, electrical outlets, *etc.* provide routes for air movement. The volume of air infiltrating or exiting in this way varies according to the tightness of fit of doors and windows, the porosity of the building shell, the height of the building, direction and velocity of wind, *etc.*

In general, the major factors controlling air leakage into or out of a building are the pressure of the wind against the structure, the temperature difference between the indoor and outdoor air, and the tightness of the building construction. Infiltration is promoted by high wind velocities and exfiltration by a low ambient temperature. In winter, the warm air within a building tends to rise and leak out of the construction. While in summer, the warm air outside tends to ingress into the building. A temperature gradient between the inside and outside of a building will draw air in at the bottom of the building (infiltration) and force air out at the top of the building (exfiltration). This process is termed the stack effect and can be of particular significance in tall buildings.

The amount of infiltration around doors and windows depends upon the quality of fit. Many windows in older buildings are poorly fitting and can result in high infiltration rates. Infiltration around doors will vary according to the type of door, room and building, but this mechanism of air movement is really only of importance for doors that are used infrequently or during the night time, when doors are generally closed.

Turner and Binnie (1990) made a comparison of carbon monoxide levels in mechanically and naturally ventilated buildings. The authors observed that externally produced carbon monoxide was present at a greater concentration in the mechanically ventilated building than the naturally ventilated building, concluding that this was likely to be due to the ingress of CO into the air handling units from underground car parks. The location of the air inlet for the ventilation system should, therefore, be a major priority when designing air conditioning systems. Kukadia and Palmer (1998)

determined very little difference between pollutant levels in naturally and mechanically ventilated buildings, with external pollutant levels being attenuated by approximately half for both the naturally and mechanically ventilated building. An investigation by Phillips *et al.,* (1993) of four naturally ventilated buildings suggested that it was likely to be the air exchange rate which was the determining factor for indoor air quality. They concluded that the greater the supply of external air, the greater the indoor concentration of external air pollutants. Colome *et al.,* (1992) in a study of domestic houses highlighted the importance of adventitious leaks for the ingress of externally produced particles in buildings with very few indoor sources.

Although a few studies have reported that indoor and outdoor particulate levels are approximately equal in buildings, without a significant indoor source (e.g. Benson *et al,.* 1972), almost all investigations into indoor:outdoor relationships for suspended particulate matter report that indoor particulate levels are, on average, lower than outdoor levels. This indicates that the shell of a building attenuates particulates which may otherwise enter the indoor environment (Colome, *et al.,* 1992). It appears from previous studies that larger particles are removed more efficiently than smaller particles (Thatcher and Layton, 1995). This is likely to be due to deposition within ventilation grills and entrapment of the particles within the building shell. Smaller particles are not removed by the building shell as efficiently, therefore, they have an indoor:outdoor ratio closer to one. What is apparent is that indoor:outdoor ratios can alter considerably from one day to the next, even when building conditions (ventilation, window and door use *etc.*) remain the same (Li and Harrison, 1990; Colome *et al.,* 1992; Thatcher and Layton,

1995). There appears to be no definite reason for this variation, although some studies suggest meteorological factors may play an important role by altering the air exchange rate of a building (Shobokshy and Hussein, 1988; Philips *et al.,* 1993).

2.3.2 Indoor:outdoor particulate matter and meteorology

Three of the main meteorological factors affecting ambient concentrations of particulate matter are wind speed, precipitation and relative humidity. As discussed in Section 2.2.4 wind direction is also very important when considering particle concentrations in street canyons. In addition, the effect of local meteorology on the air exchange rate of buildings, in terms of pressure and temperature gradients, has been discussed in Section 2.3.1. As indoor particulate concentrations are often closely dependent upon ambient concentrations, it may be assumed that any process effecting ambient concentrations will lead to a subsequent change in indoor levels.

Wind speed is a crucial factor for the re-suspension of settled dusts. Jones (1996) undertook a small scale investigation on the effects of wind speed on particulate concentrations in Birmingham, England. A positive correlation was observed between wind speed and PM_{10} during the summer. A similar relationship was also seen for the winter months, but upon closer examination of the results it was clear that this was mainly due to high concentrations of coarse particulate matter being re-suspended at very high wind speeds. This indicates that re-suspension during the winter months requires a much greater wind speed, likely to be a consequence of damp ground surface

conditions typical of British winters. In comparison, $PM_{2.5}$ demonstrated a strong negative correlation to wind speed during the summer and the winter. This is possibly because the sources of $PM_{2.5}$ are largely anthropogenic, with a high wind speed causing a dilution effect.

Relative humidity is also an important factor in the re-suspension of settled dusts. It is known that high relative humidity increases the adhesive forces acting on settled dust particles, hence a greater lifting force is required to suspend the particles into the atmosphere.

Precipitation, both solid and liquid, rapidly removes particulates from the atmosphere, with this effect often being termed precipitation or below-cloud scavenging. However, it has been suggested that once a precipitation event is over, wet deposited particulates may become re-suspended into the atmosphere so that concentrations can quickly return to previous levels (Jennings, 1998).

2.4 The chemical composition of particulate matter

Whilst the UK Department of Health Committee on the Medical Effects of Air Pollution concluded that no known chemical component of particulate matter is of a sufficient toxicity to explain the observed health effects of particulate exposure (Department of Health, 1995). It seems likely that certain particle species (e.g. sulphurous and carbonaceous particles) will have a greater influence on health than those particles with

a chemical composition similar to that of human tissue (e.g. particles mainly composed of sodium chloride). Nevertheless, the chemistry of particulate matter is important for source apportionment and is, therefore, an essential part of any research or control strategy.

Particulate chemistry has been analysed in the UK, although there appears to be no studies that have analysed for all the main chemical species together or investigated in detail any temporal or spatial variations in particulate chemistry within urban regions. Therefore, it is necessary to combine information from several studies in order to give a representation of typical particulate chemistry in the UK. The difficulty with doing this is the variations between studies in the way particulate matter has been collected and subsequently analysed. However, by combining results in this way a rough estimate of typical airborne particle chemistry can be produced. Harrison and Jones (1995) have determined typical particle chemistry in this way by combing the findings of studies performed in UK urban areas (Table 2.2).

Sulphate and nitrate are mostly anthropogenic in origin, with the fine fraction ($PM_{2.5}$) being largely accounted for by sulphate, nitrate, ammonium and carbonaceous material. Furthermore, these four species account for around half of the total mass of PM_{10}, with the remainder being from natural sources such as wind blown dust and marine aerosol. Because these species are often associated with very small particles, their indoor:outdoor ratios are often close to 1 (Li and Harrison, 1990; Lee *et al.*, 1997).

Table 2.2: Representative concentrations of individual chemical components of airborne particulate matter (Source: Adapted from Harrison and Jones, 1995)

Analyte	Typical concentrations	Typical fraction of total	Percentage found in fine fraction ($PM_{2.5}$)
PM_{10}	25-30 $\mu g\ m^{-3}$	N/A	~ 60%
TSP	35 $\mu g\ m^{-3}$	N/A	
Soluble ionic species			
Sulphate	5-10 $\mu g\ m^{-3}$	20-25 %	~ 85 %
Nitrate	2-10 $\mu g\ m^{-3}$	10-20 %	65-70 %
Chloride	1-3 $\mu g\ m^{-3}$	<10 %	~10 %
Ammonium	2-6 $\mu g\ m^{-3}$	<15 %	>95 %
Strong acid (H^+)	0.01-0.1 $\mu g\ m^{-3}$	Trace	~ 100 %
Carbonaceous			
Elemental carbon	3 $\mu g\ m^{-3}$	10 %	~ 80 %
Organic carbon	5 $\mu g\ m^{-3}$	15 %	~ 80 %
Minerals			
Insoluble minerals	~ 15 $\mu g\ m^{-3}$	20-25 %	~ 5 %
Metals			
Sodium	1 $\mu g\ m^{-3}$	2 %	21 %
Magnesium	0.1 $\mu g\ m^{-3}$	0.2 %	19 %
Calcium	0.4 $\mu g\ m^{-3}$	0.8 %	25 %
Potassium	0.1 $\mu g\ m^{-3}$	0.2 %	44 %
Lead	0.1 $\mu g\ m^{-3}$	0.2 %	~ 90 %
Other trace metals	5-50 $ng\ m^{-3}$	Trace	Most
Iron	0.5 $\mu g\ m^{-3}$	1 %	35 %
Toxic organic micro-pollutants			
Dioxins	~ 4 $pg\ m^{-3}$	Trace	Most
PCBs	~1 $ng\ m^{-3}$	Trace	Most
PAH	~150 $ng\ m^{-3}$	Trace	Most

2.4.1 Trace metals

Although trace metals only account for a small quantity of the total particulate mass, they have been extensively investigated over the past few decades due to their potential effects on human health. A summary of the sources of some trace metals is given in Table 2.3.

Lead has been historically considered the most important trace metal due to its well documented health effects, especially on young children (Brunekreef, 1986; Needleman and Gatsonis, 1990). Atmospheric lead was principally derived from the combustion of petrol containing lead additives and also from industrial smelting processes. However, since the phasing out of leaded petrol in Western Europe, emissions of lead have been greatly reduced, although some studies still show lead can be traced back to vehicle emissions (de Miguel, 1997). Municipal waste incineration can also emit relatively large quantities of lead through the escape of incinerator fly ash (Feng *et al.,* 2000). The wear of paint containing lead additives can be a significant indoor source. However, in many buildings lead paint has been removed or painted over with lead-free paint, hence this source is now far less important. Nevertheless, Feng and Barratt (1994) in a study of surface dusts in houses and offices observed that lead levels in settled dusts appear to increase with the age of a building.

Table 2.3: Summary of the sources of selected trace metals found in airborne particulate matter

Element	Sources	References
Aluminium	• Wind blown soil.	Ferguson and Kim, 1991.
Antimony	• Coal combustion. • Non-ferrous metal production. • Municipal waste incineration. • Vehicle emissions.	Huang *et al.*, 1994.
Barium	• Vehicle emissions • Municipal waste incineration. • Weathering of paint. • Wind blown soil.	De Miguel *et al.*, 1997.
Cadmium	• Many urban industrial sources. • Mainly metal smelting.	Pacyna and Munch, 1988. Hutton and Symon, 1986.
Calcium	• Wind blown soil. • Production of iron and non-ferrous metals, cement and fertiliser.	Spengler and Thurston, 1983. De Miguel *et al.*, 1997.
Copper	• Non-ferrous metal production. • Fossil fuel combustion. • Refuse incineration. • Vehicle exhaust emissions. • Paint and plastic manufacture.	Coleman *et al.*, 1991. De Miguel *et al.*, 1997. Pacyna, 1980. Mukai *et al.*, 1990.
Iron	• Wind blown soil. • Wear and tear of motor vehicles.	Ferguson and Kim, 1991.
Lead	• Vehicle emissions. • Municipal waste incineration. • Paint degradation.	De Miguel *et al.*, 1997., Feng *et al.*, 2000. Feng and Barratt 1994.
Magnesium	• Wind blown soil. • Sea spray. • Production of iron and non-ferrous metals, cement and fertiliser.	Li, 1994. Zhou, 1997.
Manganese	• Iron and steel production. • Coal combustion. • Sewage sludge incineration	Li, 1994. Zhou, 1997.
Strontium	• Wind blown soil. • Dust produced by construction and demolition.	Feng *et al.*, 2000.
Tin, cerium, rubidium and lanthanum	• Mainly natural processes. • May be related to coal combustion.	Hopke, 1980.
Zinc	• Coal combustion. • Smelting operations. • Incineration. • Wood combustion. • Vehicle tyre wear. • Vehicle exhaust emissions. • Plastic and metal fittings.	Baeyens *et al.*, 1991. Hopke *et al.*, 1980. Pacyna *et al.*, 1984. Fergusson and Kim, 1991. De Miguel *et al.*, 1997.

The main sources of atmospheric zinc are coal combustion, smelting operations, incineration, and wood combustion (Baeyens *et al.*, 1991; Hopke *et al.*, 1980; Pacyna *et al.*, 1984). Vehicle tyre wear has been shown to contribute significantly to the zinc level in street dust, but is mainly associated with coarser particles (Stigliani and Anderberg, 1991; Fergusson and Kim, 1991). De Miguel *et al.,* (1997) also suggests that zinc is related to exhaust emissions from motor vehicles. They suggest that this is because zinc compounds are often found in engine lubricating oils as detergents and to aid dispersion. Indoor sources of zinc include the degradation of plastic and metal fittings often found inside buildings (Culbard *et al.*, 1988). In the UK, average annual emissions of zinc were around 3400 tonnes in the period 1979 to 1983, with the top three contributors being metal production, waste incineration, iron and steel industries, which on average emitted 1620, 970 and 480 tonnes of zinc into the air, respectively, in each year (QUARG, 1993).

The main sources of copper are non-ferrous metal production, fossil fuel combustion and refuse incineration. In the UK, the main source of atmospheric copper is fossil fuel combustion (Coleman *et al.*, 1991). De Miguel *et al.,* (1997) has also observed that copper can be related to vehicle exhaust emissions. Other sources include paint and plastic manufacture (Pacyna, 1980). A catalyst filtering system containing copper has been developed for reducing particulate emissions from heavy duty diesel vehicles (Transport Research Laboratory, 1994). They suggested that if this system was used on buses then it could become a major source of atmospheric copper in urban areas. In addition, with many cars now fitted with catalytic converters containing platinum,

palladium and rhodium, there is concern that emissions of these metals could increase as a result of exhaust system wear (Mukai *et al.*, 1990; Hudge and Stallard, 1986).

One of the most important data sources of trace metal composition of particulate matter in the UK is the Department of the Environment's Multi-Element Survey (DoE, 1995), which has been in operation since 1976. Five urban areas were chosen for use in the survey: Central London, London Borough of Brent, Leeds, Motherwell and Glasgow. A M-type sampler was used to collect particulate matter in this survey. Upton and Barrett (1985) evaluated the collection efficiency of this sampler and found that it had a good collection efficiency for particles smaller than 4 μm, but above this diameter its performance was erratic. Annual average concentrations of trace metals measured during the survey between 1984 and 1993 are shown in Table 2.4.

Table 2.4: Trace metal concentrations (ng m^{-3}) measured in Central London between 1984 and 1993 (Source: DoE, 1995)

Metal	84/85	85/86	86/87	87/88	88/89	89/90	90/91	91/92	92/93
Cadmium	2.8	3.6	2.7	7.2	16	4.8	1.3	<1	0.4
Chromium	12	5.5	10	14	15	11	4.3	6	5.4
Copper	27	27	-	32	34	25	28	24	13
Iron	980	840	940	1000	1100	1140	1687	913	891
Manganese	19	18	17	18	18	20	25	15	21
Nickel	17	7.8	8.6	8.8	10	8.9	8.6	5	5.2
Zinc	100	94	93	94	120	111	139	65	59
Vanadium	32	14	14	14	16	15	20	15	12
Cobalt	-	-	-	-	2.2	0.8	0.8	-	0.3
Lead	480	270	280	300	220	-	120	99	78

Another long term study is the AEA-Technology atmospheric elements survey (Lee *et al.*, 1994). This study involved urban sites in the following areas: Walsall (West Midlands), Trafford and Manchester (Greater Manchester), Brent and Lambeth (Greater London). The samplers used in this survey consisted of a polyethylene sampling head comprising an inlet duct, filter holder and cover, a small mains operated pump connected to a standard gas meter (Cawse and Peirson, 1972). Garland and Nicholson (1991) found that under typical wind conditions only particles of less than a few microns in diameter could be collected by this sampler with an acceptable efficiency. Selected results obtained during this survey are summarised in Table 2.5.

Table 2.5: Summary of data from the AEA Technology trace element survey for the Walsall, UK site (Source: Lee *et al.*, 1994)

Element	Mean ($ng\ m^{-3}$)	Standard Deviation	Minimum	Maximum
Ag	5.3	3.8	0.2	23.2
Al	838	282	246	1481
As	93.9	89.7	10.6	572.3
Br	155	89	35	483
Cd	28.3	24.5	0.2	93.1
Ce	1.07	0.62	0.23	3.43
Cl	6216	2284	1700	11371
Cr	24.9	10.2	6.1	62.3
Fe	1687	833	790	5484
Hg	0.54	0.41	<0.01	2.02
Na	1447	624	184	3251
Ni	31.2	22.2	1.4	109
Pb	1316	577	360	3094
Sc	0.263	0.181	0.08	1.005
Se	16.7	10.1	0.5	42.3
Sm	0.086	0.053	0.005	0.231
V	21.2	11.1	6.3	51
Zn	2634	1325	254	6155

There have also been several short term studies of atmospheric particulate trace metal concentrations in the UK (Lin, 1988; Cutajar, 1995; Harrison *et al.*, 1996). The concentrations of trace metals found in these studies have been consistent with the results of the surveys described above.

2.4.2 Sulphate, nitrate and chloride

The majority of sulphate in airborne particles is found in the fine fraction and originates from secondary atmospheric reactions of SO_2 (Monn and Sachaeppi, 1993).

$$SO_2 + H_2O \longrightarrow H_2SO_3 \qquad \text{Eqn. (2.5)}$$

$$H_2SO_3 + H_2O_2 \longrightarrow H_2SO_4 + H_2O \qquad \text{Eqn. (2.6)}$$

$$H_2SO_3 + O_3 \longrightarrow H_2SO_4 + O_2 \qquad \text{Eqn. (2.7)}$$

The H_2SO_4 aerosols can react either with NH_3 to form small crystals of $(NH_4)_2SO_4$ or with other airborne particles (sea salts, wind blown dust, etc.) to form metallic salts:

$$H_2SO_4\,(l) + 2NH_3\,(g) \longrightarrow (NH_4)_2SO_4\,(s) \qquad \text{Eqn. (2.8)}$$

$$H_2SO_4\,(l) + 2NaCl\,(s) \longrightarrow Na_2SO_4\,(s) + 2HCl\,(g) \qquad \text{Eqn. (2.9)}$$

$$H_2SO_4\,(l) + CaCO_3\,(s) \longrightarrow CaSO_4\,(s) + CO_2\,(g) + H_2O\,(g) \qquad \text{Eqn. (2.10)}$$

Since gaseous ammonia exists abundantly in the atmosphere, Eqn. 2.8 is often the dominant process, depending on solar input.

Direct emissions of sulphate to the air are mainly associated with the combustion of sulphur containing fossil fuels. It has also been reported that diesel engine vehicles emit particulate matter with a sulphate concentration as high as 14% (Lowenthal *et al.*, 1994).

Nitrate and nitric acid originate principally from photochemical oxidization reactions of NO_2. The following reactions explain the predominant conversion processes (Harrison *et al.*, 1994).

$NO_2 + OH \longrightarrow HNO_3$	(day time)	Eqn. (2.11)
$NO_2 + O_3 \longrightarrow NO_3 + O_2$	(night)	Eqn. (2.12)
$NO_2 + NO_3 \rightleftharpoons N_2O_5$	(night)	Eqn. (2.13)
$N_2O_5 + H_2O \longrightarrow 2HNO_3$	(night)	Eqn. (2.14)
$NO_3 + RH \longrightarrow HNO_3 + R$	(night)	Eqn. (2.15)

Once formed, HNO_3 reacts with NH_3, atmospheric salt or other existing particles in the air to form nitrate particles (e.g. Pio *et al.*, 1992; Harrison *et al.*, 1994; Wu and Okada, 1994; Pakkanen, 1996).

$NH_3 + HNO_3 \rightleftharpoons NH_4NO_3$	(fine particles)	Eqn. (2.16)
$NaCl + HNO_3 \longrightarrow NaNO_3 + HCl$	(coarse particles)	Eqn. (2.17)

In the atmosphere ammonia and nitric acid are normally present below the required levels for the formation of particulate ammonium nitrate. Therefore, during these conditions, Eqn. 2.17 becomes the predominant process resulting in a permanent removal of nitric acid from the atmosphere (Harrison *et al.*, 1994; Mehlmann and Warnek, 1995).

Particulate nitrate can also be formed by reactions of NO_2 with sea salt and mineral particles (Mamane and Gottlieb, 1989 and 1992):

$$2NO_2\,(g) + NaCl\,(s) \longrightarrow ClNO\,(g) + NaNO_3\,(s) \qquad \text{Eqn. (2.18)}$$

$$SO_2\,(g) + 2O_2\,(g) + 2NaCl\,(s) \longrightarrow Na_2SO_4\,(s) + 2ClO\,(g) \qquad \text{Eqn. (2.19)}$$

Mamane and Gottlieb (1992) also found that the rates of the above reactions can be significantly enhanced by UV light.

In coastal regions, the majority of particulate chlorides originate from marine aerosols, with particles from this source being found mainly in the coarse fraction (Hara *et al.*, 1989). In inland areas coal combustion and refuse incineration can release large quantities of gaseous HCl which then reacts with ammonia or other alkaline particles to form ammonium and metallic chlorides.

$$HCl\,(g) + NH_3\,(g) \rightleftharpoons NH_4Cl\,(s) \qquad \text{Eqn. (2.20)}$$

Particulate chlorides produced by this process are mainly in the fine fraction (Lightowlers and Cape, 1988). During winter, re-suspension of rock salt applied to roads can also cause very high concentrations of chloride in the urban atmosphere (Willison *et al.*, 1989), with particles from this source tending to be in the coarse fraction.

The depletion of particulate chlorides has been observed under certain atmospheric conditions (Harrison and Pio, 1983; Clegg and Brimblecombe, 1985). This is caused by absorption of SO_2 and NO_X onto NaCl aerosols, causing them to oxidise to H_2SO_4 and HNO_3. Willison *et al.*, (1989) observed that higher temperatures, slow moving and well mixing air facilitate the displacement of particulate chlorides.

There have been several studies conducted to determine the anion content of airborne particulate matter in the UK. These have been in Leeds (Clarke *et al.*, 1984; Willison *et al.*, 1989), Lancaster (Colbeck and Harrison, 1984; Harrison and Pio, 1983), Essex (Harrison and Allen, 1990) and Birmingham (Harrison *et al.*, 1996). Table 2.6 summarises the typical concentrations of sulphate, nitrate and chloride in the UK atmosphere measured in these studies.

Table 2.6: A summary of sulphate, nitrate and chloride concentrations in the UK atmosphere

Location	Sampling Date	Size Fraction	Mean Concentration ($\mu g\ m^{-3}$)			Reference
			SO_4^-	NO_3^-	Cl^-	
Leeds	10/82 to 09/83	$PM_{2.5}$	6.6	1.2	0.8	Willison *et al.*, 1985
		PM_{10}	1.0	0.9	1.2	
Haverah Park	10/82 to 09/83	$PM_{2.5}$	5.8	1.6	0.6	Willison *et al.*, 1985
		PM_{10}	0.6	0.7	0.9	
Lancaster	10/78 to 11/78	TSP	7.27	5.96	-	Colbeck *et al.*, 1984
	09/79 to 10/79	TSP	9.23	3.6	-	
Essex	08/86 to 11/86	TSP	3.46	3.06	0.89	Harrison *et al.*, 1990
	02/87 to 04/87	TSP	9.34	9.14	2.27	
	05/87 to 12/98	TSP	5.4	-	-	
Birmingham	01/92 to 02/92	$PM_{2.5}$	5.25	1.26	0.27	Harrison *et al.*, 1996
		PM_{10}	1.14	0.67	0.76	
	07/92 to 08/92	$PM_{2.5}$	2.89	0.81	0.024	
		PM_{10}	0.51	0.85	0.61	

2.4.3 Organic compounds

About one third of the carbonaceous material present in airborne particles is present as elemental carbon and the remaining two thirds as organic compounds (Harrison and

Jones, 1995; Gray *et al.*, 1986). These organic compounds are often present as normal alkanes (N-Alkanes), aliphatic acids, aromatic carboxylic acids and polynuclear aromatic hydrocarbons (PAHs). PAHs are normally present at very low concentrations, but because of their potential health effects, they have been extensively investigated (Bodzec *et al.*, 1993; Jaffrezo *et al.*, 1994; Raiyani *et al.*, 1993; Clayton *et al.*, 1992).

Fossil fuel combustion is the most significant anthropogenic source of atmospheric PAHs. It has also been shown that particles emitted by diesel engines contain PAHs in the solvent organic fraction of the particulates (Williams *et al.*, 1989). Other anthropogenic sources of PAHs include industrial and domestic heating systems, refuse burning and tobacco smoke (Nikolaou *et al.*, 1984). The aromatic content of fuel plays a major part in PAH production and displays a linear relationship with particle bonded PAH emissions (Nikolaou *et al.*, 1984). The average emission rates of total hydrocarbons from a light duty petrol vehicle are approximately 2-3 times greater than a heavy duty diesel vehicle. However, the emissions of nitro derivatives of PAH are consistently higher from diesel engines (Van den Hout and Rijkeboer, 1986). Although the actual amounts of PAHs produced also depend on air-fuel ratio, type of engine lubricant, driving mode, age of vehicle, engine speed, load and torque (Pedersen *et al.*, 1980). Hewitt and Rashed (1990) found that diesel engines emit far higher quantities of fluoranthene, benzo(a)anthracene, chrysene, benzo(a)pyrene, and benzo(ghi)perylene than petrol engines (Table 2.7). Because vehicle exhaust emissions are a significant source of PAHs, this can lead to elevated concentrations at kerbside locations.

Goldstone (1990) also measured ambient PAH concentrations at a kerbside location in London between 1986 and 1987 (Table 2.8).

Table 2.7: Emission rates of some selected PAH compounds (Source: Hewitt and Rashed, 1990)

Compound	Petrol Vehicle ($\mu g\ km^{-1}$)	Diesel Vehicle ($\mu g\ km^{-1}$)
Phenanthrene	91.0	--
Anthracene	28.0	--
Fluoranthene	20.5	36.4
Pyrene	21.6	16.3
Benzo(a)anthracene / Chrysene	4.3/0.3	10.2
Benzo(a)pyrene	0.7	2.4
Benzo(ghi)perylene	1.2	<2.5

Table 2.8: Roadside concentrations of PAHs (Goldstone, 1990)

Compound	Concentration ($ng\ m^{-3}$)	
	Winter	Summer
Phenanthrene	0.15	<0.05
Anthracene	0.3	0.1
Fluoranthene	1.3	0.4
Pyrene	1.3	0.4
Benzo(a)anthracene	1.25	0.4
Chrysene	2.0	0.5
Benzo(b)fluoranthene	2.2	1.0
Benzo(k)fluoranthene	1.0	0.5
Benzo(a)pyrene	2.1	0.3
Benzo(ghi)perylene	4.0	2.9
Indeno(123-cd)pyrene	2.0	1.3

PAHs in the atmosphere are present in both gaseous and particulate forms. PAHs more volatile than phenanthrene are normally only present in the gas phase, whilst

phenanthrene and fluoranthene can be present in both gas and particulate phases. PAHs less volatile than pyrene are usually found in the particulate phase.

PAHs often found in airborne particulate matter include phenanthrene, methylphenanthrene, anthracene, fuoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(e,a)pyrene, benzo(b,k)fluoranthene, indino(1,2,3-cd)pyrene, benzo(g,h,I)perylene and coronene. However, the relative concentrations of these PAHs can vary between seasons and locations (Leuenberger *et al.*, 1988; Bodzek *et al.*, 1993).

Only a few groups of atmospheric toxic organic compounds have been extensively investigated in the UK. The Department of the Environment's Toxic Organic Micro-pollutants Network (TOMPs) has measured dioxins, polychlorinated biphenyls (PCBs) and PAHs at four urban locations of Cardiff, London, Manchester and Stevenage since 1991 (QUARG, 1996). Baek *et al.*, (1992) and Harrison *et al.*, (1996) have also analysed PAHs in London and Birmingham, respectively.

2.4.4 Indoor:outdoor chemical relationships of particulate matter

The indoor:outdoor ratios for different chemical species is highly variable. Those chemical species with an indoor source normally possess an indoor:outdoor ratio greater than one.

Particle diameter is the most important factor when considering chemical indoor:outdoor relationships. This is because fine particles normally penetrate into buildings with greater efficiency than larger, coarse particles. Wallace (1996) concluded that particles within the PM_{10} size fraction could penetrate a building with the same efficiency as non-reactive gases, therefore, those chemical species associated with small particles often have an indoor:outdoor ratio closer to unity than those species associated with larger particles.

The indoor:outdoor ratio for sulphate is often very close to unity, usually in the range of 0.8 to 0.9 (Li and Harrison, 1990; Lee *et al.*, 1997). It is also generally agreed that sulphate is found almost entirely in fine particles and is unlikely to be found in high quantities in particles greater than about 2.5 μm in diameter (Clayton *et al.*, 1992; Jones, *et al.*, 2000). Jones *et al.*, (2000) also found that indoor:outdoor ratios for sulphate decreased with increasing particle size (0.9 for $PM_{1.1}$ and 0.5 for PM_{10}), suggesting much more efficient ingress of very fine than coarser particles into the building.

The indoor:outdoor ratios for elemental species are also closely related to particle diameter, for example, calcium and iron often have very low indoor:outdoor ratios as these elements are normally associated with coarse particles. However, elements such as zinc, bromine and lead can have higher indoor:outdoor ratios as these elements are associated with finer particles, with ratios for these elements normally being in the 0.5 to 0.6 range (Alzona *et al.*, 1979; Jones *et al.*, 2000). Jones *et al.*, (2000) measured a

decrease in the indoor:outdoor ratio with increasing particle size similar to sulphate for lead, although the relationship was not as pronounced.

2.5 Particle number concentration

In many epidemiological studies particle number concentration has not been measured, therefore, the relationships between number concentration and mortality is unclear. As epidemiological research has determined a linear relationship between PM_{10} mass concentrations and mortality, it may be expected that particle count measurements would show a similar relationship. Routine measurements of particle number have only recently started at a few locations in the UK, and in most countries is not measured at all (Harrison *et al.,* 1999).

In terms of acute respiratory symptoms, one study observed certain lung function parameters of asthmatics being more strongly associated with the number of ultrafine particles <0.1 μm than PM_{10} (Peters and Wichmann, 1996), however, another study found no association (Pekkanen *et al.,* 1997).

Clean marine air has been found to have particle counts of approximately 200 particles/cm^3, whereas, measurements in streets have found particle counts of around 30,000 - 50,000 particles/cm^3 (QUARG, 1996). These previous findings illustrate the impact of anthropogenic sources upon particle count. This impact is far greater for particle count than for particulate mass where natural sources can be very important.

From a study in Birmingham, England, Harrison *et al.,* (1999) concluded that particle number count is a far better indication of traffic generated particulate matter than PM_{10}. They suggested that this was due to PM_{10}, showing diurnal fluctuations, which are influenced by non-traffic factors, such as re-suspension.

2.6 Mineral magnetics and airborne particulate matter

2.6.1 Summary of magnetic behaviour

The origins of magnetic properties found in any substance are held within the atoms of which it is composed. The behaviour of electrons in the atom enables them to spin on their own axes as well as orbit the nucleus of the atom. It is the action of both of these spins that produces a magnetic moment (Smith, 1999). It is this magnetic phenomenon, occurring at the atomic scale, which is responsible for controlling the entire magnetic behaviour of a substance. As a result, the various combinations of atoms and molecules that form the structure of substances promote distinct magnetic properties or magnetic signatures. It is these magnetic properties of individual substances that contribute to the overall magnetic properties of a material composed of various substances with different magnetic properties.

There are three types of recognised magnetic behaviour, including diamagnetic, paramagnetic, and ferromagnetic. Ferromagnetic includes the sub-categories anti-

ferromagnetic, ferrimagnetic and canted anti-ferromagnetic. A general summary of the types of magnetic behaviour is presented in Table 2.9.

Atomic and crystallographic structures exert only a partial control on the behaviour and existence of magnetic materials. This is because ferromagnets are also controlled by magnetic domains, defined by Smith (1999) as being regions of parallel atomic magnetic moment in a crystal. This means that magnetic domains represent regions inside the structure of a material, which can be magnetised in a particular direction. Consequently, magnetic domains are influenced by the shape and size of magnetic domains within a crystal and by the boundaries between neighbouring magnetic domains. The three principal forms of magnetic domains in ferromagnetic materials are multidomain (MD), stable-single-domain (SSD) and superparamagnetic (SP). Smith (1999) provides a more detailed explanation of magnetic domains.

Those variables used to characterise the mineral magnetic properties of environmental materials and an explanation of their interpretation are presented in Table 2.9. All of the variables summarised in Table 2.9 are used in this research.

Table 2.9: Magnetic variables their basic interpretations (Source: Maher, 1988 and Walden *et al.*, 1996)

Magnetic variables	Interpretations
χ	Mass specific *Magnetic Susceptibility* (χ): This is measured within a small magnetic field and is reversible (no remanence is induced). Its value is roughly proportional to the concentration of ferrimagnetic minerals within the sample, although in materials with little or no ferrimagnetic component and a relatively large antiferromagnetic component, the latter may dominate the signal.
ARM	Mass specific *Anhysteretic Remanent Magnetisation* (ARM): For this work ARM was induced in the samples by combining a peak AF field of 100mT with a DC biasing field of 0.04mT. It is particularly sensitive to the concentration of magnetic grains of SSD size, e.g. *ca.* 0.03 - 0.06μm.
SIRM	Mass specific *Saturation Isothermal Remanent Magnetisation* (SIRM): This is the highest amount of magnetic remanence that can be produced in a sample by applying a large magnetic field. It is measured on a mass specific basis. In this study a saturating field of 0.8T has been used and will produce saturation in most mineral types. However, some antiferromagnetic minerals may not be saturated in this field (e.g. goethite) and therefore this parameter is often called IRM_{800mT}. The value of SIRM is related to concentrations of all remanence-carrying minerals in the sample but is also dependent upon the assemblage of mineral types and their magnetic grain size.
Magnetisation variables (forward field ratios) i.e. %soft and %hard	It is instructive to calculate the percentage of the final SIRM acquired at selected, increasing field strengths. Forward field ratios are shown against a horizontal scale of percentage saturation at 20mT ($100(IRM_{+20mT}/SIRM)$) and 300mT ($100(IRM_{+300mT}/SIRM)$). These values help discriminate between ferrimagnetic and imperfect antiferromagnetic mineral types, since the latter are likely to be the main contributors to remanence acquired above the second field. The amount of remanence acquired in an initially demagnetised sample after it has experienced a field of 20mT. At such low fields, the magnetically 'hard' canted antiferromagnetic minerals such as haematite or geothite are unlikely to contribute to the IRM, even at fine grain sizes. The value is therefore approximately proportional to the concentration of the magnetically 'softer' ferrimagnetic minerals (e.g. magnetite) within the sample, although also grain sizes dependent. At high fields of 300mT, the magnetically 'soft' ferrimagnetic minerals are likely to have been saturated and any subsequent growth of IRM will be due to magnetically 'harder' canted antiferromagnetic component within the sample. The value is approximately proportional to the concentration of canted antiferromagnetic minerals (e.g. haematite and geothite) within the sample.
Backfield Ratios i.e. S-ratio (IRM_{-100mT})	Various demagnetisation parameters can be obtained by applying one or more reversed magnetic fields to a previously saturated sample. The loss of magnetisation at each backfield can be expressed as a ratio of $IRM_{backfield}$/SIRM, and therefore gives a result between +1 and -1 normalised for concentration. Such ratios can be used to discriminate between ferrimagnetic and canted antiferromagnetic mineral types. For example, using the 100mT backfield ratio, minerals which are relatively easy to demagnetise (e.g. magnetite) have relatively low values (referred to as 'soft' magnetic behaviour). Minerals that show a stronger resistance to demagnetisation (e.g. haematite) show relatively high 100mT backfield ratios (referred to as 'hard' magnetic behaviour).
ARM / χ	The ratio of these variables can indicate the concentration of ferrimagnetic grain size variations (e.g. a high ratio indicates the presence of SSD grains).
SIRM / ARM	In samples dominated by ferrimagnetic minerals, the ratio of these variables is indicative of relative magnetic grain size variations (e.g. low ratio indicates the presence of SSD grains).
SIRM / χ	The ratio of these variables can be diagnostic of either magnetic mineralogy (e.g. a low ratio might indicate paramagnetic minerals, and a high ratio might indicate the importance of haematite or geothite) or where samples have similar mineral types and concentrations, it can be diagnostic of magnetic grain size variations (e.g. a high ratio indicates SSD ferrimagnetic grains, and a low ratio indicates the importance of superparamagnetic (SP) or multidomain (MD) grains).

2.6.2 Mineral magnetic measurements and airborne particulate matter

Many studies of airborne particulate matter and street dust focus on elemental concentrations, organic constituents and source identification. However, since Oldfield *et al.,* (1985) demonstrated that non-destructive magnetic measurements can be of use in characterising atmospheric dust sources, other researchers have shown relationships between magnetic properties, heavy metal content and organic content. Xie *et al.,* (1999) have expanded upon this earlier work to show how magnetic properties vary with particle size.

Magnetic particles can be found in vehicle emissions. Iron often occurs as an impurity in fossil fuels; during vehicle combustion carbon and organic material are lost by oxidation, whilst the iron forms a non-volatile and magnetic spherical residue (Matzka and Maher, 1999). These spherules contain variable amounts and a range of particle sizes of magnetite (Fe_3O_4) and/or haematite (Fe_2O_3). It has also been shown that vehicle emissions simultaneously release hazardous substances and magnetic particles. Morris *et al.,* (1995) showed a strong correlation between sample mutagenicity and magnetic susceptibility for respirable particulate matter collected at a road side location. In addition to particles formed during the combustion process, non-spherical magnetite particles can also be produced via engine and vehicle body wear (Olson and Skogerboe, 1975). Hoffmann *et al.,* (1999) demonstrated the relationship between vehicle emissions and magnetic susceptibility by mapping the magnetic enhancement of surface soil

adjacent to a motorway in Germany. Maximum values were recorded within 2-5 m of the edge of the road and reflected the prevailing wind direction.

A study of urban dusts in the centre of Munich (Matzka, 1997) identified a strong correlation between magnetic concentration (measured by its saturation remnant magnetisation - SIRM) and total PM_{10} mass. In this study a strong correlation between SIRM and PM_{10} mass ($R^2 = 0.879$) indicated a coexistence of magnetic and other urban dust particles.

From these previous studies, it appears that it may be possible to use magnetic measurements to determine the degree of vehicle derived particulate contamination in a given location.

2.7 Summary of literature and aims

From previous studies of the indoor:outdoor relationships of particulate matter, it is clear that indoor:outdoor ratios can vary widely on a day to day basis, even when building use and ventilation remains constant (Shobokshy and Hussein, 1988; Li, 1994 and Colome *et al.,* 1992). The reasons for this are largely unknown, although many researchers suggest meteorological factors are likely to contribute to this variation. Shobokshy and Hussein (1988) demonstrated that meteorological variables can play a key role in determining indoor:outdoor relationships. They formulated an empirical model predicting indoor concentrations from outdoor concentrations, using the mean

wind speed and mean atmospheric pressure for a 24 hour period. Further research into this area is required to further understand the relationships between meteorology and indoor:outdoor ratios, especially for buildings located with street canyons. A wider range of meteorological factors such as ambient temperature, wind direction and precipitation, as well as wind speed and atmospheric pressure, also require examination. In addition, as most people spend the majority of their time indoors, it is expected that outdoor concentrations, indoor concentrations and meteorological factors can be related to personal exposure. Seasonal variations in indoor:outdoor ratios also need researching as this area appears to have received minimal attention. Mainly because the majority of indoor and outdoor measurements are only performed on a short term basis or as sporadic measurements.

Although there has been a large quantity of research conducted on the dilution and movement of vehicle generated pollutants inside street canyons, there appears to have been very few studies on what effects this has upon the concentrations of vehicle derived pollutants inside buildings forming the canyon. Because indoor particulate concentrations are often related to outdoor concentrations, it seems likely that buildings within street canyons will contain higher concentrations of vehicle derived pollutants than those buildings not situated within a canyon. Therefore, building occupants will be exposed to greater pollutant concentrations during their residence inside the building.

Dust can exist in two main phases, settled dust and airborne particulate matter. In terms of indoor air quality, settled dust can be either dust deposited on to surfaces outdoors,

such as street dust, or dust deposited on to indoor surfaces such as floors and other surfaces. It is clear that both forms of settled dust are a potential source of airborne particulate through re-suspension, even though the causes of re-suspension may be different. Airborne particulate matter is also a source of settled dust through deposition. The relationships between settled dust and airborne particulate matter are relatively unclear and mainly hypothetical, requiring further research to discover if any significant relationships exist.

Routine measurements of particle number have only recently commenced in the UK and other countries, therefore, the relationships between particulate mass and particle number are unclear and require further investigation. There is also very little published literature taking into account the indoor to outdoor relationships of particle count. Due to the small diameter of the particles measured by particle counters, a clear relationship between outdoor particle number and indoor particle number would be expected as it would be expected that small particles would penetrate indoors with a high efficiency.

A holistic approach was taken to this research incorporating the measurement and analysis of both settled dust (indoors and outdoors) and airborne particulate mass concentration as well as particle count. Airborne particulate matter and settled dusts were collected and analysed at various locations and for several time scales to satisfy the main aims of the research as outlined below:

- Determine how indoor particulate concentrations are affected by a buildings proximity to a busy road, and the subsequent effect that this has upon the personal exposure of building occupants.

- Analyse airborne particulate matter, street dust and indoor dust for anions and metals to determine likely sources of the dust.

- Assess the relationships between local meteorological conditions and the penetration of particulates from outside to inside.

- Determine the inter-relationships between settled dust outdoors, settled dust indoors and airborne particulate matter in an indoor environment using chemical analysis of the different phases of dust.

- Determine the relationships between gravimetric particulate concentration and particle number concentration, both indoors and outdoors.

- Assess how the relationship between gravimetric particulate concentration and particle number concentration is affected by a building's proximity to a busy road.

- Use mineral magnetic measurements of sampled street dust as a method of identifying the input of vehicle emissions to a specific location.

Chapter 3

Materials and Methods

3.1 Introduction

In this chapter the methods will be described which were used in the collection, measurement and analysis of airborne particulate matter, settled dust (dust deposited on raised surfaces indoors), street dust and indoor dust. This includes the determination of particulate matter concentrations using filter papers and automatic instruments and the methods used to characterise settled dust by scanning electron microscopy. The sampling and magnetic/chemical analysis of indoor dust and street dust are also explained.

The collection of all indoor airborne particulate samples and those samples connected with settled dust were made away from areas of the room containing heating equipment, doors and ventilation units. Photocopiers, fax machines and computer equipment were also avoided.

Local meteorology was recorded at the University of Wolverhampton urban meteorological station located on the rooftop of Building Three. The mean daily precipitation quantity and the mean daily rainfall duration for the sampling period was 4.13 mm and 2.58 hours, respectively. Therefore, for the purpose of data interpretation days were classified as either having zero precipitation, low precipitation or high

precipitation. Low precipitation included those days with a quantity of precipitation of less than or equal to 4.13 mm (the average daily rainfall during the sampling period). High precipitation was all those days with a quantity of precipitation greater than 4.13 mm. Similar categories were also used for rainfall duration, with low rainfall duration being those days with less than or equal to 2.58 hours of precipitation (the average rainfall duration throughout the sampling the sampling period). High precipitation was those days with rainfall duration greater than 2.58 hours. These categories were chosen to give sufficient data in all the categories to allow statistical analysis of the results.

3.2 Sampling location descriptions

3.2.1 Road Descriptions

The collection of street dust was undertaken at three roads within the West Midlands. Two of the three roads are located in Wolverhampton City Centre, with the third road a residential road in nearby Dudley approximately 10 km away from Wolverhampton City Centre. This road was selected as it is in an area with low traffic flow and no local industry.

3.2.1.1 Road One (Lichfield Street, Wolverhampton: Grid reference SO 916 987)

This road is the main approach road to the primary bus station in Wolverhampton City Centre (Plate 3.1). The road is closed to vehicles except buses, taxis and service vehicles

so buses contribute almost 100% of the traffic using the road, with approximately 10,000 of them using the route each day (Source: Wolverhampton City Council Environmental Health). Traffic is held up at traffic lights at one end of the road regularly causing queues of vehicles idling along the entire stretch of road. Four and five storey buildings on both sides of the road, and a relatively narrow width of 21 m, produce a small street canyon effect, which may impede the dispersion of traffic related emissions. Previous work has demonstrated that high concentrations of airborne particulate matter exist alongside this road (Giess, 1998).

Plate 3.1: View of road one showing typical daytime traffic levels

3.2.1.2 Road Two (Wulfruna Street, Wolverhampton: Grid reference SO 914 988)

Situated in Wolverhampton City Centre and located 200 m away from Road One, this road is only occasionally used by heavy duty vehicles, does not carry high traffic flows

and the buildings do not produce any significant street canyon effect (Plate 3.2). No traffic data is available for this road. A DEFRA background air quality monitoring station is located at one end of the road.

Plate 3.2: View of Road Two

3.2.1.3 Road Three (Meadow Road, Dudley: Grid reference SO 924 988)

Road Three is a residential road located in a sub-urban area of Dudley, located approximately 1.5 km away from Dudley Town Centre and 10 km away from Wolverhampton City Centre (Plate 3.3). The road is very infrequently used by heavy duty vehicles and generally carries very low traffic flows. No traffic data is available for this road. This particular road was chosen for ease of access and to represent a non-city centre, urban road in contrast to Roads One and Two.

Plate 3.3: View of Road Three

3.2.2 Building Descriptions

Figure 3.1: Relative locations of the three main sample buildings (Extract from Ordnance Survey OS map)

Settled dust, indoor dust and airborne particulate matter were collected and analysed inside three buildings, namely Building One, Building Two and Building Three. The buildings are owned by the University of Wolverhampton and are located in Wolverhampton City Centre. Indoor dust was also collected at a residential house in Dudley, termed Building Four and is located on Road Three. The relative locations of Building One, Two and Three are shown in Figure 3.1. Buildings One and Two are located on opposite sides of Road One.

For part of the sampling the three foyers of Buildings One, Two and Three were used. The foyers were chosen to represent broadly similar indoor environments as all three have doors opening directly onto the road and they all have a similar throughput of people. In addition, all of the buildings are located within 200 m of one another in Wolverhampton City Centre. However, there are several differences that exist between the foyers. Firstly, Building One is not located in any form of canyon, unlike Buildings One and Two, and there is substantially less traffic using the road outside Building One. This allows the foyer of Building One to be considered a control as it does not have the effects of a street canyon or heavy duty diesel vehicles immediately outside, unlike Buildings One and Two. The location of the foyers allows the examination of two important factors on particulate levels in the foyers. Firstly, the effect of the street canyon and secondly the effect of the diesel buses using the road between Buildings One and Two.

3.2.2.1 Building One

Two areas within this building were used for measurements and sample collection. Firstly, a histology laboratory measuring 3 m x 7 m x 3 m, selected because the room is very rarely used meaning that physical disturbance is kept to a minimum (Plate 3.4). This room is located at ground level with sash style wooden windows, measuring 1m x 1.5 m, that opens onto Road One. Although the windows can be opened, they remained closed for the duration of this research. There is only one door opening into the room, which remained permanently locked when samples were not being collected. All woodwork inside the room had recently been re-painted with lead-free paint. A study by Giess (1998) indicated that high concentrations of airborne particulate matter exist in this room.

The second room inside Building One used for sample collection was the buildings main foyer, measuring 24 m x 16 m x 6 m (Plate 3.5 and Figure 3.2). Settled dust, indoor dust, chemical deposition rate and measurements of airborne particulate matter were investigated here. The foyer has a double door system opening onto Road One, with the first door being permanently open during the daytime, although both doors are closed throughout the night. The second door is kept closed but the large throughput of people using this building means the door is in regular use. The building façade is situated 3 m from the kerbside with a concrete pavement between the building and the kerb, however due to the shape of the building this distance varies slightly along the length of the building.

Plate 3.4: Histology laboratory

Plate 3.5: The main foyer of Building One

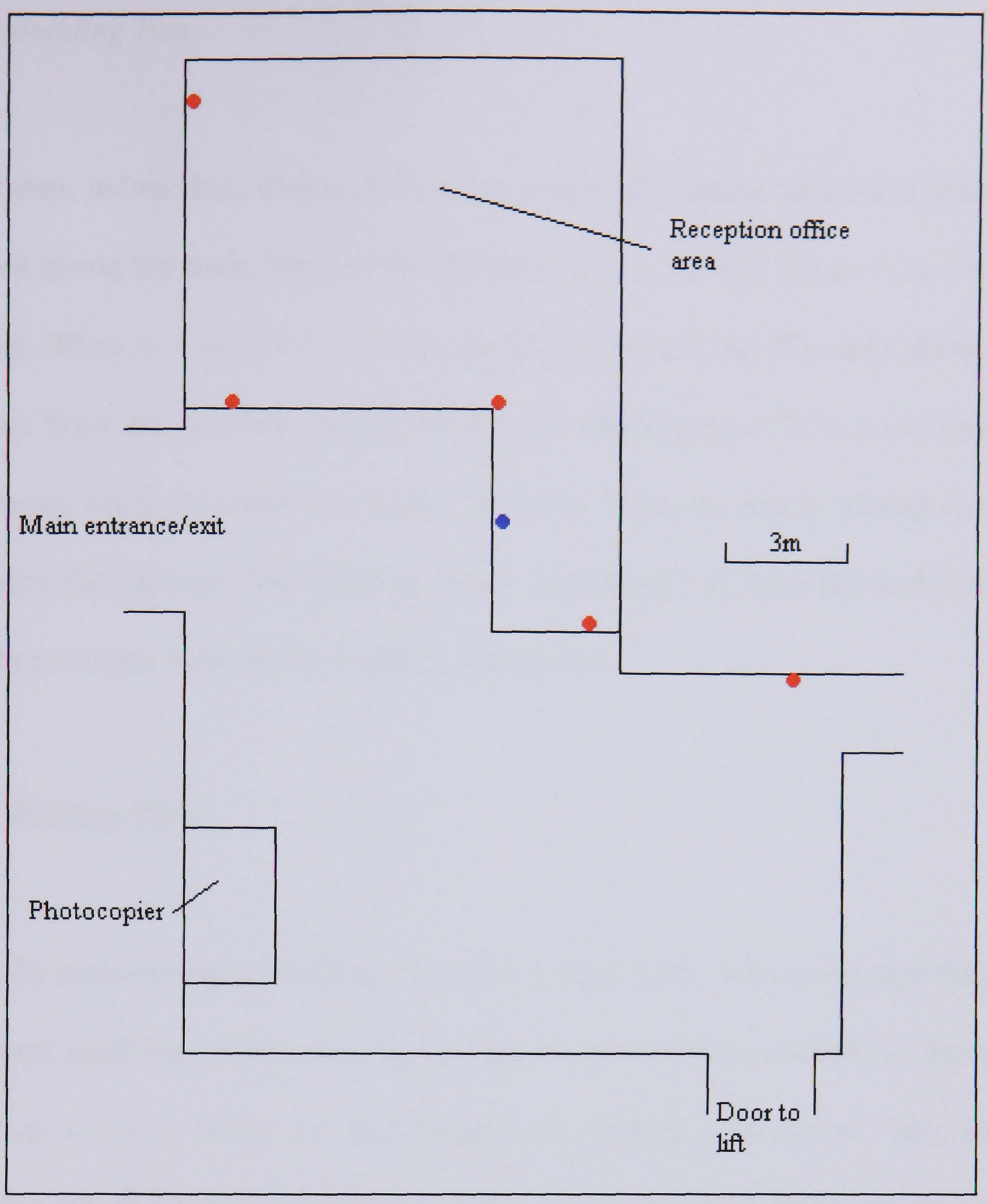


Figure 3.2: Plan of main foyer inside Building One (location of sampling points for settled dust, chemical deposition rate and dust soiling rate measurements are indicated by a red dot. Blue dot indicates location of respirable particulate sampler)

3.2.2.2 Building Two

Settled dust, indoor dust, chemical deposition rate and airborne particulate matter were collected inside the main foyer of this building (Plate 3.6 and Figure 3.3). This room measures 20 m x 7 m x 3.5 m. Also located on Road One the main doors to this buildings foyer are relatively poorly fitted, with visible gaps of 2 to 3 mm around the door frames when the doors are closed. The main doors are also in almost continuous use during the daytime. The building façade is situated 3 m from the kerbside with a concrete pavement between the building and the kerb.

3.2.2.3 Building Three

This is the main University building, located on Road Two, with a very high throughput of students, staff and visitors walking through the foyer. Dimensions of this foyer are 20 m x 8 m x 3.5 m (Plate 3.7 and Figure 3.4). Settled dust, indoor dust, chemical deposition rate and airborne particulate matter were collected in this foyer. There is also a cafeteria on the floor below where a small amount of cooking is performed. This foyer is different to that of Buildings One and Two as the main doors do not open directly on to the road outside. The entrance to this foyer is located down a wide stairwell. A double door system is incorporated into this building, with the outer door being permanently open during the daytime and both doors closed at night. The main reason for selecting this building was in a contrast to Building One and Two, as although it is located in Wolverhampton City Centre there is no obvious immediate effect from traffic. The

building façade is situated 3 m from the kerbside with a concrete pavement and very small areas of planted shrubs between the building and the kerb.

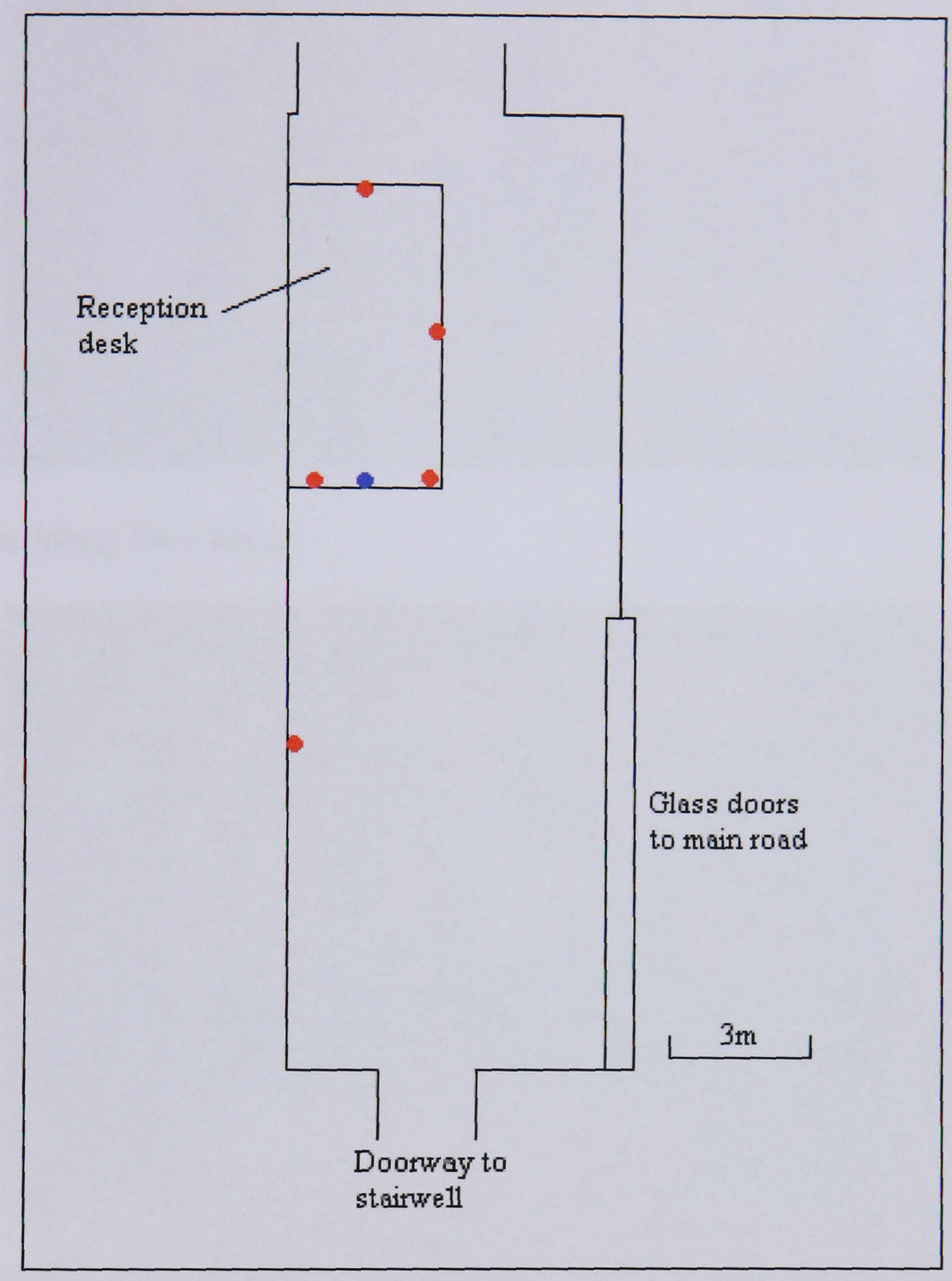


Figure 3.3: Plan of main foyer inside Building Two (location of sampling points for settled dust, chemical deposition rate and dust soiling rate measurements are indicated by a red dot. Blue dot indicates location of respirable particulate sampler)

Plate 3.6: Building Two foyer

Plate 3.7: Building Three foyer

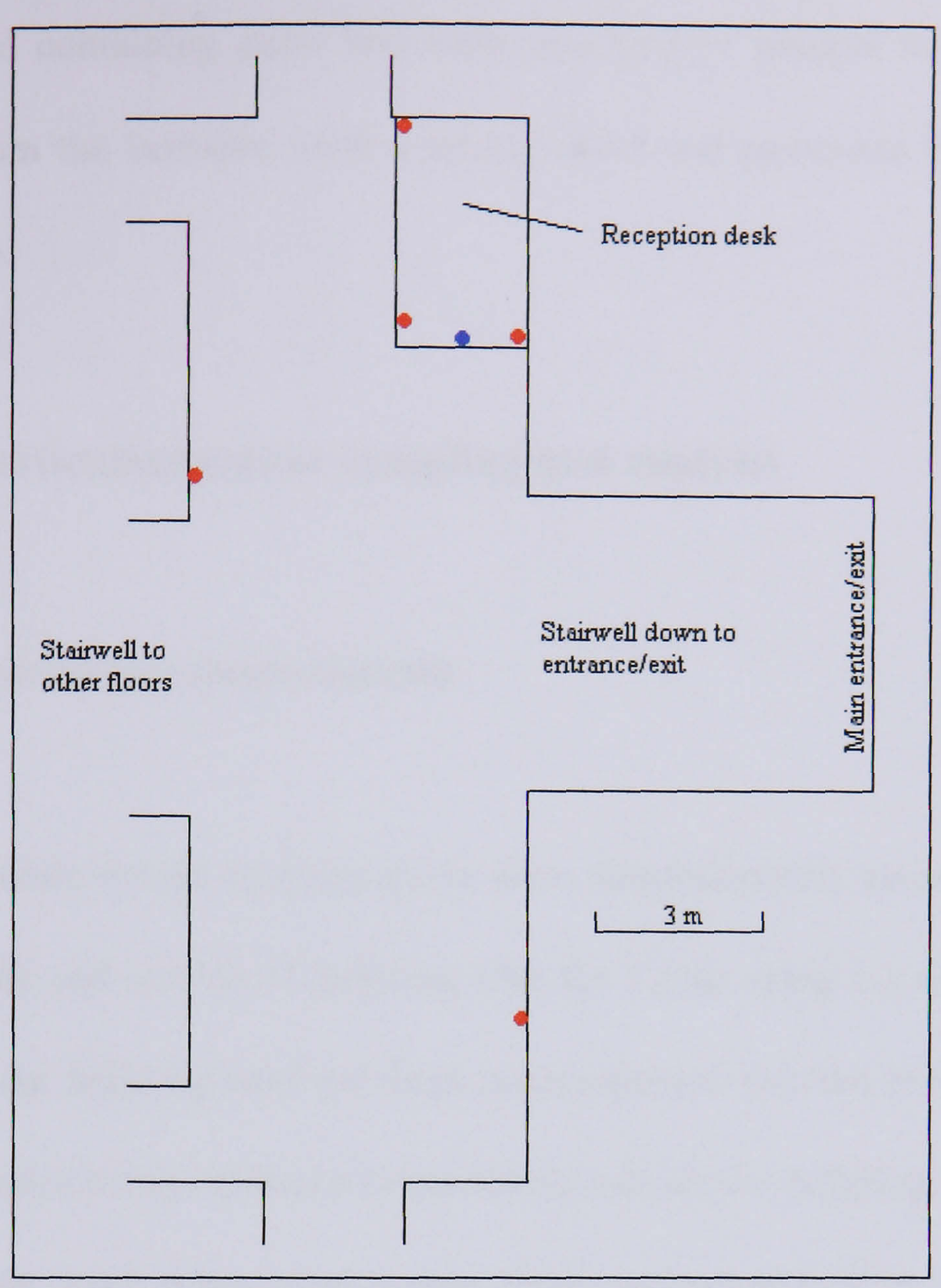


Figure 3.4: Plan of main foyer inside Building One (location of sampling points for settled dust, chemical deposition rate and dust soiling rate measurements are indicated by a red dot. Blue dot indicates location of respirable particulate sampler)

3.2.2.4 Building Four

Building Four is a traditional three bedroom, semi-detached house built in the 1930s located in Dudley, West Midlands. Indoor dust was collected from all rooms within the house. The entire house had been renovated approximately one year prior to sampling;

therefore, all lead containing paint had been removed or painted over. The building façade is 9 m from the kerbside, with a tarmac drive and pavement between the front door and the kerb.

3.3 Airborne particulate matter sampling and analysis

3.3.1 Airborne particulate measurements

Respirable particulate matter concentrations were simultaneously recorded for 24 hour time periods inside and outside of Building One for 1 year using a gravimetric method. The room inside the building used for these measurements was the histology laboratory with outdoor samples being collected immediately outside the building, approximately 5 m further along the road at the same height above ground at 0.50 m. Total suspended particulate matter, PM_{10} and $PM_{2.5}$ were also collected at these indoor and outdoor locations. To enable a good comparison outdoor particulate samples at the other roads were also collected from a height above ground of 0.50 m.

Respirable particulate concentrations were measured simultaneously inside the three foyers for a period of approximately 4 months. Measurements of TSP, PM_{10} and $PM_{2.5}$ were also made inside the three foyers at a height of 1.20 m. In addition, a height profile of respirable particulate concentrations was recorded for Building One foyer, with simultaneous measurements being recorded at 0.15 m, 2.00 m and 3.50 m above floor level.

To assess the variation of respirable particulate concentrations within the street canyon formed by the Buildings along Road One, gravimetric particulate measurements were recorded simultaneously at roof top level and ground level on both sides of the road.

Ultrafine particle count and real time PM_{10} measurements were measured inside and outside the three buildings using real time monitors with a data logging facility.

3.3.2 Filter preparation and gravimetry

Casella Vortex sampling pumps were used to obtain all the gravimetric measurements of TSP, PM_{10}, respirable particulate concentrations and $PM_{2.5}$. Fitting the pumps with various sampling heads enabled the collection of the different size categories of particulate onto a filter paper. Although there are many other designs of particulate sampling equipment for the collection of airborne particles, the basic principle of operation is the same. The mass of the collected aerosol is determined by weighing the filter before and after exposure. The difference between the two measurements is divided by the sampled air volume to obtain the mass concentration.

In the Casella aerosol sampling system for the collection of PM_{10}, $PM_{2.5}$ and respirable particulates a cyclone head was used to separate the larger particles from the smaller particles, achieved by centrifugation. The smaller particles are collected on the filter paper (either 25 mm or 37 mm in diameter), while the larger particles deposit into a

rubber grit pot from where they are discarded. The same type of cyclone is used to collect all three size categories of particulates and is size selective dependent upon the flow rate through the cyclone. The flow rates used for the sampling of PM_{10}, $PM_{2.5}$ and respirable particulates are show in Table 3.1. For the collection of TSP a different sampling head is used, within which no size selection occurs.

Table 3.1: Flow rates used by the Casella aerosol sampling system for the collection of PM_{10}, $PM_{2.5}$ and respirable particulates.

Particle Size	D50 cut-off µm	Required flow rate l min^{-1}
Thoraic	10	1.0
Respirable	4	2.2
$PM_{2.5}$	2.5	3.5

The flow rate, depending upon the size of particles to be collected, was set at the beginning of each sampling period and then confirmed at the end. If the flow rate had altered by greater than 5%, the sample was discarded. Because simultaneous measurements were taken using different cyclone heads, it was necessary to ensure the results were comparable and that there were no discrepancies between measurements taken with different cyclones. All the cyclones used in the sampling were run alongside one another for 48 hours and the concentrations of particles recorded on each filter paper determined, this was repeated several times. A *t*-test showed no significant difference (n = 20) between the particles collected by each cyclone (Figure 3.5).

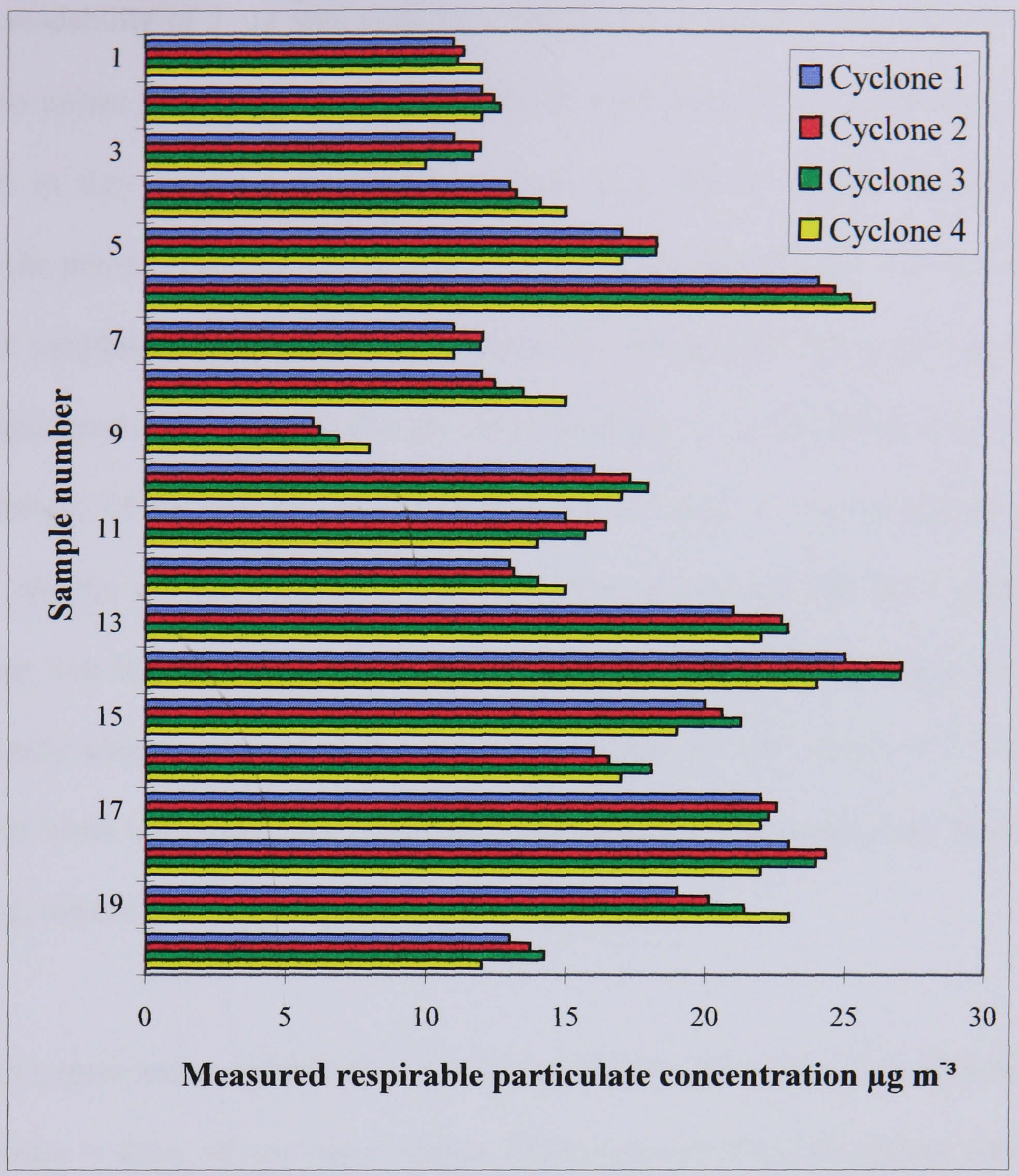


Figure 3.5: Comparison between the four cyclone heads used for sampling

Generally, with gravimetric analysis, it is necessary to condition the filter papers in a dessicator before and after use so that humidity will not affect the weight. The extent to which this is required is dependent upon the type of filter paper used during collection. The majority of samples were taken using 37 mm and 25 mm glass fibre filter papers (Whatman GF/A), however, the suitability of Nucleopore (etched polycarbonate) and cellulose nitrate filter papers was also assessed. A Mettler Toledo MT5 micro-balance

with a readability of 1 μg was used to weigh all filter papers. Both Nucleopore and cellulose nitrate filter papers were found to be unsuitable for the collection of most samples as they caused a significant pressure drop during particle collection. This caused the pump drawing air through the filter to automatically stop, meaning that full 24 hour sampling periods could not be achieved. Nucleopore filter papers also suffer from significant static electrical charges (Engelbrecht *et al.,* 1980), which made accurate measurement of the weight impossible. Even after using a static eliminator, which should remove all electrostatic charge, the filter papers still carried a charge and weighing was highly inaccurate. In many cases, the negative weight induced by the electrostatic charge outweighed the particulate loading so that exposed filter weighed less than when unexposed. As glass fibre filter papers do not suffer from electrostatic charging, the use of a static eliminator was not required.

All filter papers were conditioned in a sealed container with silica gel for 48 hours prior to exposure to drive off any water vapour. After exposure, the filter papers were again conditioned for 48 hours and re-weighed. The re-weighing of blank, conditioned glass fibre filter papers on different days, gave values that were repeatable to within ±1 μg, this degree of error was between 0.25% and 2% of a typical particle loading of between 50 and 250 μg. The re-weighing of blank glass fibre filter papers, which were simply stored in the laboratory and not inside a sealed container, also gave values repeatable to within 1 μg. However, exposed filter papers may contain particles that are hydrophilic, leading to an increase in filter weight due to water adsorption. The conditioning of filter papers was, therefore, continued throughout the sampling regime, with filters only being

removed from the container for a few seconds prior to weighing. Unexposed control filters were stored with the samples and these were also weighed to identify any change in mass due to humidity. None of these control filters showed a change in mass greater than ± 2 μg.

Table 3.2: The effect of filter washing upon respirable particle retention efficiency ($\mu g\ m^{-3}$) on glass fibre filter papers

Sample Number	Measured by unwashed filter	Measured by washed filter	Difference (+ -)
1	25	26	+1
2	12	10	-2
3	39	41	+2
4	21	22	+1
5	8	9	+1
6	22	20	-2
7	15	16	+1
8	24	24	0
9	32	30	-2
10	28	29	+1
11	36	35	-1
12	11	11	0

Because the collected particles were to be analysed for chemical composition, following the final weighing of the filters, they were then stored at 4° C to prevent the loss of volatile species. Unavoidable exposure of the filters to room temperature occurred whilst the filter papers were being conditioned for weighing. In addition, because glass fibre filter papers can contain high amounts of impurities, prior to the filter papers being used for particle collection, a washing regime was used to make chemical analysis more accurate. Before being used for sample collection the glass fibre filter papers were first conditioned by being soaked in nitric acid for 2 hours and then left in a bath of de-ionised water for 24 hours. The filter papers were then rinsed in copious amounts of de-

ionised water and allowed to dry in a sealed container with silica gel. The filters were then removed from the container and stored in closed petri dishes until being required for use. Control experiments showed that the washing of filter papers by this method did not decrease particle retention efficiency (Table 3.2). Analysis of the filter papers showed that this washing procedure greatly reduced the background concentrations of all the elements analysed (Table 3.3). Concentrations of anions on the blank filter papers were negligible, even for unwashed filter papers.

Table 3.3: The effect of filter washing on blank elemental concentrations of glass fibre filter papers

	Mean concentration (ppm)	
Element	Before washing	After Washing
Aluminium	0.9252	0.4626
Calcium	2.2734	1.0003
Cadmium	0.0094	0.0027
Cobalt	0.0037	0.0011
Chromium	0.0946	0.0378
Copper	0.0182	0.0071
Iron	0.9943	0.4772
Mercury	0.0037	0.0010
Potassium	2.9713	0.7131
Lithium	<LOD	<LOD
Magnesium	0.0194	0.0062
Mangenese	0.0142	0.0067
Molybdenum	0.0103	0.0033
Sodium	16.1304	3.7100
Nickel	0.0732	0.0322
Phosphorus	0.1409	0.0634
Lead	0.5988	0.1736
Selenium	0.0411	0.0156
Strontium	<LOD	<LOD
Titanium	0.0288	0.0127
Vanadium	0.0032	0.0014
Yttrium	0.0026	0.0006
Zinc	3.8678	1.8179
Zirconium	0.0581	0.0232
n = 12, SE always less than 5% of the mean.		

3.3.3 Personal exposure measurements

Personal respirable particulate measurements were also taken for one non-smoking individual who worked inside Building One. The sample inlet was at approximate breathing height (shoulder level). Samples were collected for a total of 23 working days with indoor and outdoor measurements recorded simultaneously. The sampling duration for the indoor, outdoor and personal exposure measurements was 8 hours between 0900 and 1700 hours. This length of time was chosen in order to coincide with the average working day. The subject was asked to keep a diary of activity, indicating the length of time spent outdoors and whether they came into contact with any strong source of particulate matter, such as tobacco smoke or cooking. The subject came into contact with such sources for extended time periods on three of the sample days. These samples were, therefore, considered unrepresentative and were discarded. Examination of the activity log for the individual showed that on average only 35 minutes of the 8 hour working day (7.5 %) was spent outside the building.

3.3.4 Other particulate sampling techniques

Although the majority of particulate measurements were made gravimetrically, results using other aerosol sampling techniques have also been used, including the Casella Microdust real time monitor and the P-Trak ultrafine particle counter. The Casella Microdust measures and records PM_{10} concentrations while the P-Trak counts particles

in the size range 0.2 μm to 1 μm. The operation of these sampling techniques is described below.

3.3.4.1 Casella Microdust

The Casella Microdust 880nm was used to measure and record PM_{10} concentrations both indoor and outdoors. This measuring device is capable of recording PM_{10} concentrations between 1 μg m^{-3} and 2500 μg m^{-3}. The instrument uses a modulated beam of infrared light projected forwards into the measuring chamber. Under conditions of zero airborne particulate concentrations all the infrared light is prevented from reaching the receiver by a light stop. When suspended dust enters the chamber, the light beam is scattered forward within a narrow angle to the receiver. The instrument then calculates the PM_{10} concentration from the quantity of light detected by the receiver.

3.3.4.2 P-Trak ultrafine particle counter

The P-Trak ultrafine particle counter is capable of counting particles in the size range 0.02 to 1 μm up to a concentration of 5 x 10^5 particles cm^{-3}. Airborne particulate matter is drawn into the equipment, using a built in pump. Upon entering the instrument, particles pass through a saturator tube where they mix with a vapour of isopropyl alcohol. The particle/alcohol mixture is then drawn into a condenser where alcohol condenses onto the particle surface, causing them to grow in size and allowing them to be counted. The droplets then pass through a laser beam, producing flashes of light. The

light flashes are sensed by a photo-detector and counted to determine particle number concentration. A simplified schematic diagram of the P-Trak ultrafine particle counter is illustrated in Figure 3.6.

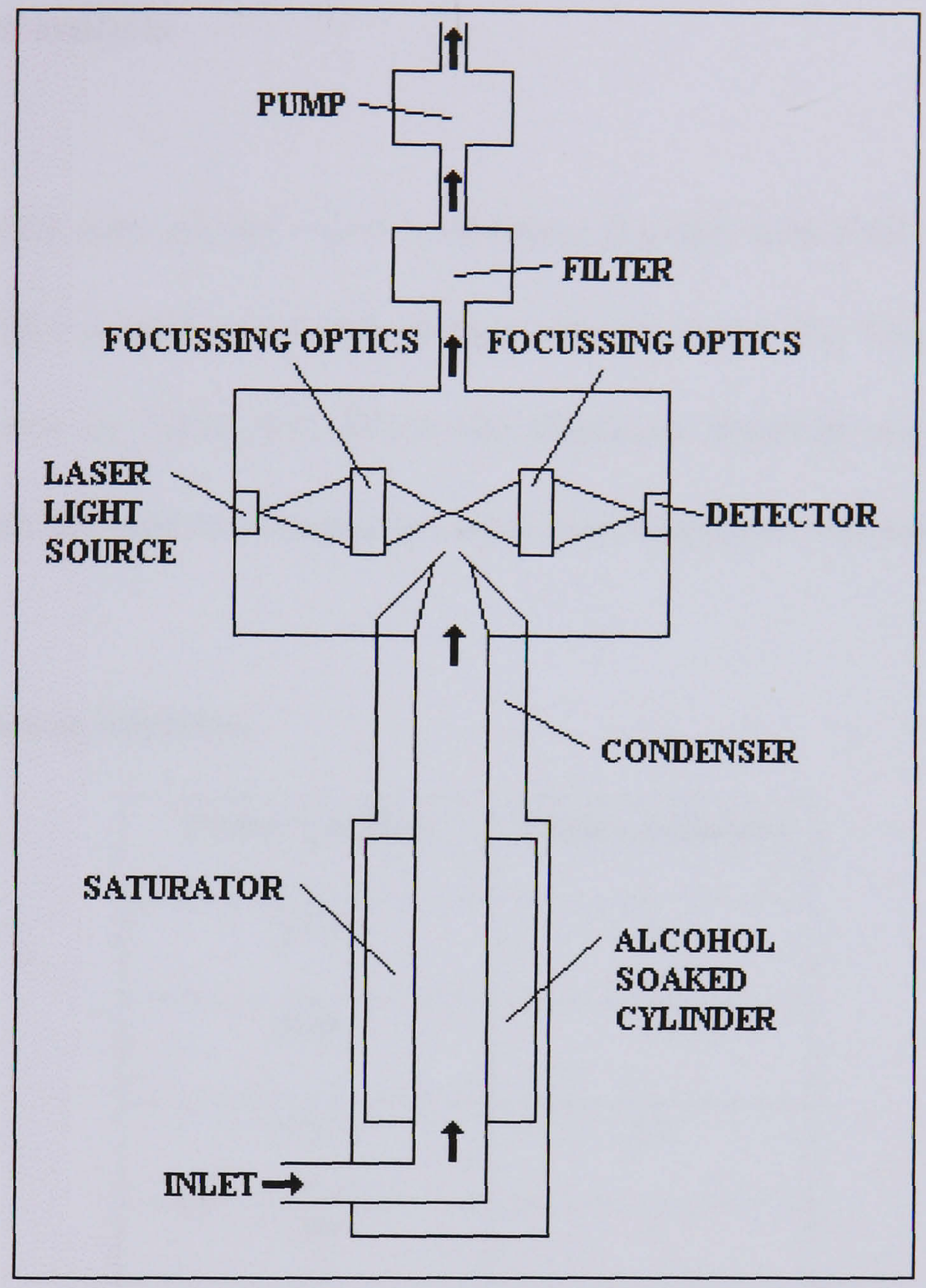


Figure 3.6: Schematic diagram of the P-Trak ultrafine particle counter

3.3.5 Chemical analysis of airborne particulate matter

For both anionic and elemental determination, blank values were obtained by extracting and analysing 10 un-exposed filter papers of the same type and from the same batch.

Blank values of anions were generally found to be negligible, whilst blank elemental concentrations were not sufficiently large to interfere with the analysis.

3.3.5.1 Elemental analysis

Loaded filter papers were closed vessel microwave digested with 8 ml of sulphuric acid, 4 ml of hydrochloric acid and 2 ml of hydrofluoric acid. The times and power of digestion is shown in Table 3.4. When the digestion duration was completed, the samples were then allowed to cool and the microwave digestion was repeated.

Table 3.4: Digestion duration

Power (watts)	Time (minutes)
250	6
400	6
650	12
250	6

The samples were then made up to a volume of 25 ml in acid washed volumetric flasks with de-ionised water. The solution was then shaken vigorously and allowed to settle in a refrigerator for a minimum of 48 hours to allow any particles in the solution to settle to the bottom of the flask. The solution was then decanted and analysed for a suite of elements by inductively coupled plasma atomic emission spectrometry (ICP-AES).

3.3.5.2 Anion analysis

The filters for anion analysis were extracted into 10 ml of de-ionised water and mechanically agitated to ensure thorough removal of the particulates. To aid dissolution, 1 ml of propan-2-ol was added. Concentrations of chloride, sulphate and nitrate ions were determined using a Dionex DX100 Ion Chromatograph.

3.3.6 Scanning electron microscopy of airborne particulate matter

Scanning electron microscopy was undertaken on a selection of respirable particulate matter samples. The aim of this was to look at visual differences between samples taken at various locations, indoors and outdoor, so that any differences in the structure of particles could be observed.

Using the Casella Vortex Personal Samplers particles were collected on Nucleopore polycarbonate filters with a pore size of 0.2 μm. These filters have a very smooth surface, therefore the image is not confused by the structure of the filter material. A Camscan SV2 electron microscope was used for all imaging.

Following particulate collection sections of the loaded filter paper were mounted on carbon SEM stubs and attached in place with a small amount of carbon adhesive. The samples were then coated in a gold sputter before being photographed in the SEM. A visual comparison was then made between samples from different locations.

3.3.7 Diesel particulate collection and analysis

3.3.7.1 Diesel particulate collection

It is generally accepted that the chemical composition and the quantity of particulate emitted from diesel engines is dependent upon engine type/design, running speed, engine temperature, fuel mixture and load. In addition, the type of fuel and engine oil can also have an effect.

Searle (2001) collected diesel particulate matter for use in another University of Wolverhampton research project. He overcame the variations in emitted particulate matter due to the reasons above, by collecting particulate matter from a total of 24 single and double-decker buses at various engine speeds and operating temperatures.

In order to collect a large quantity of diesel particulate a piece of equipment was developed to facilitate direct exhaust collection (Searle, 2001). The particulate could then be transferred into a suspension of deionised water for storage prior to analysis.

The collector consisted of a wooden box containing a number of glass plates, staggered both vertically and horizontally to form a series of baffles. During sample collection the box is sealed and a negative pressure induced using a wet/dry vacuum cleaner. This causes the exhaust gas to be drawn through the 150 mm stainless steel inlet pipe and into the box. As the gas is forced to change direction around the glass baffles particulate

is deposited onto the glass surface. The sampling protocol is summarized below (Searle 2001) and a description of all the buses used for sample collection is given in Table 3.5:

1. Vehicle engine was started and allowed to idle until normal operating temperature was reached (taking approximately 15 minutes).
2. Cleaned and autoclaved glass plates were inserted into the collecter.
3. Engine revolutions were increased to maximum (approximately 1700 RPM) and held sustained.
4. Vacuum was turned on.
5. Engine revolutions were dropped to idling speed for 10 seconds and then raised back to maximum.
6. Steps 3 to 5 repeated at 2 minute intervals.
7. Particulate was collected for 20 minutes.
8. Glass plates were removed from the collector and transferred to the laboratory for removal of particulate into suspension within two hours.
9. One impaction plate was placed face down into a 'KERRY' model PUIS 250 ultrasonic bath.
10. 500 ml deionised water was added to bath and the bath turned on for 15 minutes.
11. The plate was removed from the bath and any remaining particulate adhering to the glass was washed back into the bath using a minimum quantity of deionised water.

12. All the remaining plates are placed into the bath one at a time and steps 10 and 11 repeated.
13. The diesel suspension was then transferred into a brown glass Winchester and stored at 4° C.

Table 3.5: Model of diesel engine used in particulate collection (Source: Searle, 2001)

Registration number	Double or single-decker	Engine type	Sample date
POG 491Y	D/D	Gardner 6LXB, 10.45 L, 6 cylinder	24/11/1997
GOG 265W	D/D	Gardner 6LXB, 10.45 L, 6 cylinder	02/12/1997
POG 489Y	D/D	Gardner 6LXB, 10.45 L, 6 cylinder	18/02/1998
A672 VOE	D/D	Gardner 6LXB, 10.45 L, 6 cylinder	18/02/1998
NOA 442X	D/D	Gardner 6LXB, 10.45 L, 6 cylinder	09/03/1998
B807 AOP	D/D	Gardner 6LXB, 10.45 L, 6 cylinder	13/03/1998
B873 DOM	D/D	Gardner 6LXB, 10.45 L, 6 cylinder	13/03/1998
F80 XOF	D/D	Gardner 6LXB, 10.45 L, 6 cylinder	20/03/1998
BOK 42G	D/D	Gardner 6LXB, 10.45 L, 6 cylinder	03/04/1998
LOA 331X	D/D	Gardner 6LXB, 10.45 L, 6 cylinder	03/04/1998
KJW 289W	D/D	Gardner 6LXB, 10.45 L, 6 cylinder	03/04/1998
BOK 43V	D/D	Gardner 6LXB, 10.45 L, 6 cylinder	08/04/1998
LOA 416X	D/D	Gardner 6LXB, 10.45 L, 6 cylinder	08/04/1998
KJW 289W	D/D	Gardner 6LXB, 10.45 L, 6 cylinder	08/04/1998
ROX 640Y	D/D	Gardner 6LXB, 10.45 L, 6 cylinder	08/04/1998
G106 FJW	S/D	Metro Camel, Weynmann Ltd	21/04/1998
GOG 265W	S/D	Metro Camel, Weynmann Ltd	21/04/1998
GOG 196W	S/D	Metro Camel, Weynmann Ltd	21/04/1998
N133 WOV	S/D	Volvo B10B, 'Wright Endurance'	29/04/0998
POG 497Y	D/D	Gardner 6LXB, 10.45 L, 6 cylinder	29/04/0998
LOA 392X	D/D	Gardner 6LXB, 10.45 L, 6 cylinder	19/05/1998
G114 FJW	D/D	Gardner 6LXB, 10.45 L, 6 cylinder	19/05/1998
GOG 152W	D/D	Gardner 6LXB, 10.45 L, 6 cylinder	19/05/1998
POG 494Y	D/D	Gardner 6LXB, 10.45 L, 6 cylinder	19/05/1998

When particulate collection was complete, the particulate solutions were mixed together and the mass per unit volume was calculated. This was achieved by evaporating a sample of the solution with a known mass at 40° C and weighing the residue. A total of 6.73 g of diesel particulate was collected and held in suspension with 8.043 l of deionised water.

3.3.7.2 Chemical analysis

The diesel particulates were analysed for anionic and elemental content. For anion analysis a sample of the suspension was first filtered and analysed for chloride, nitrate and sulphate concentrations using a Dionex DX100 Ion Chromatograph. Blank anion concentrations of the deionised water used to make the suspension were also measured, all of which being below the limit of detection of the instrument.

For elemental analysis the particulates first had to be removed from suspension. This was achieved by evaporating the suspension inside a sealed container with silica gel until a residue of diesel particulates weighing 0.5 g had been collected. The residue was then microwave digested with 8 ml of sulphuric acid, 4 ml of hydrochloric acid and 2 ml of hydrofluoric acid using the same digestion method as shown in Table 3.4 and made up to a volume of 25 ml with deionised water. The digested solution was then filtered through acid washed glass fibre filter papers prior to analysis by ICP-AES. To assess the quantity of analytes that had been lost into the deionised water whilst the particulates were stored in suspension, a sample of the suspension was also analysed. The

concentrations measured in the suspension were generally less than 1% of the concentrations determined from the particulates removed from suspension. Only the relatively reactive elements Na and K showed greater than a 1 % loss into the suspension, but both were still under 5 %.

Loss on ignition, as first described by Ball (1964), was used to determine the quantity of combustible organic material present. Three samples each weighing 1 g were subjected to the loss on ignition test. The samples were oven dried at 105° C for 24 hours, weighed and then heated to 375° C for 16 hours and re-weighed to determine the loss on ignition.

3.4 Settled dust sampling and analysis methods

3.4.1 Dust soiling rate measurements

The measurement of dust soiling rates was achieved by using 5 pre-weighed glass microscope slides coated in a thin, even layer of grease (petroleum jelly) to prevent the removal of dust from the slide during collection, transport and subsequent weighing. To ensure an even layer of grease the slide was gently heated at 105° C until the grease had melted evenly over the slide surface. Post-weighing of the slides enabled the determination of dust soiling rates in mg m^{-2} day^{-1}. Ten control slides left in dust free enclosures, open to the air, demonstrated that weight loss due to evaporation or drying of the grease was minimal, with the mean weight loss being less than 0.1 mg for a

period of one month. Slides spiked with a known quantity of dust showed that there was no measurable loss of dust during transport or weighing of the slides. Therefore, any error in the gravimetric measurements can be assumed to be less than 0.1 mg, being less than 5% of a typical dust loading of 2 to 3.5 mg. All weighing of glass slides was performed on a Mettler Toledo micro-balance with a readability of 0.1 mg. The locations of the slides inside the building foyers were away from radiators and air conditioning outlets/inlets. Cleaning staff were also instructed not to interfere with the slides. The cleaning regime is the same for each of the buildings and does not alter throughout the year. Therefore, the exposure environments of the slides from building to building were almost identical.

3.4.2 Collection of settled dust for SEM analysis

Settled dust for analysis by SEM (Camscan SV2) and EDX (Link Analytical) was collected on carbon SEM stubs with carbon low contaminant spectro-tabs attached (Supplied by Agar Scientific, Stansted, UK). The spectro-tabs are weakly adhesive on both sides hence they easily attach to the stubs and once dust particles settle, they adhere to the surface of the tab. Each stub was left in the appropriate location at approximately 1.5 m above ground for one month to enable the collection of sufficient dust for analysis.

3.4.2.1 SEM analysis of settled dust

Using SEM, measurements of particle size, aspect ratio and chemistry (determined semi-quantitatively by EDAX) were made of particles on each stub. For individual particle analysis, all particles were randomly selected. Particle size and aspect ratio was measured by obtaining an image of 202 individual particles from each stub. Image analysis software (Scion Image 4.72) was then used to measure the particles and to determine aspect ratio. For 100 of these particles elemental content was determined semi-quantitatively by EDAX. The Link Analytical EDX used for this analysis is capable of analysing for all elements with an atomic mass greater than neon.

3.4.3 Chemical deposition rate measurement

Glass petri dishes were left open in the main foyers of Buildings One, Two and Three for one month. After this time the dishes were sealed for transportation back to the laboratory. Three petri dishes were used for the measuring of anion deposition rate and three were used for determining elemental deposition rates. Chemical deposition rates were determined in this way during winter months (December, January and February) and during summer months (June, July and August) to assess variation due to location and any seasonal differences.

The dust, which had collected in the petri dishes, was transferred onto pre-weighed glass microscope slides to determine the quantity of collected dust. All weighing was performed on a Mettler Toledo MT5 microbalance with a readability of 1 μg. The dust for elemental deposition rate measurements was microwave digested with 4 ml of sulphuric acid, 2 ml of hydrochloric acid and 1 ml of hydrofluoric acid and made up to a volume of 15 ml with deionised water. The time and power of digestion is shown in Table 3.4. The solutions were then allowed to settled in a refrigerator for 48 hours before being decanted and analysed by ICP-AES.

For anion deposition rates the dust was removed from the petri dishes and weighed in the same manner, mixed with 10 ml of de-ionised water and 1 ml of propan-2-ol. The solutions were then mechanically agitated for 24 hours before analysis of chloride, nitrate and sulphate by a Dionex DX100 Ion Chromatograph.

3.5 Street dust sampling and analysis methods

Three roads were chosen for the collection of street dust. Road One is the road located between Building One and Building Two. Road Two is the road running outside Building Three and Road Three is in a sub-urban residential area mostly unused by heavy duty diesel vehicles and generally carrying low traffic flows.

3.5.1 Street dust sample collection

The length of each road was measured and 6 equally spaced samples were taken along the length of the road. Samples were collected in the centre of the pavement with all dust material being collected from an area of 1 m^2. The dust was collected by brushing with a small paint brush. Samples were taken on a monthly basis on the 15th of each month for a period of one year, unless ground conditions were damp, in which case the collection was undertaken as soon as the pavements had dried. Samples were either taken late at night or early in the morning to allow the maximum time possible to elapse between the time pavements were swept by street cleaners and when samples were collected. The samples were then visibly examined and any plant, hair and animal material was removed. Following the visual screening samples were dried in an oven for 48 hours at 105° C. Each sample was then passed through a series of sieves to separate the dust into the following size fractions; 0-63 μm, 64-90 μm, 90-180 μm and 180-250 μm. These size fractions were chosen as particles smaller than 90 μm can be suspended into the atmosphere. Particles larger than 90 μm are likely to be transported by saltation or creep (de Miguel *et al.,* 1997). However, it is also considered important to analyse the larger particle size ranges as the larger particles may degrade over time and become smaller in diameter.

Dust from each size classification for each sample was then divided into three sub-samples for elemental, anion and percentage organic analysis. For the size category 0-63

μm magnetic properties were measured for the same sub-sample used for percentage organic analysis.

3.5.2 Street dust chemical analysis

3.5.2.1 Elemental analysis

From each street and from each size category a 250 mg dust sample was microwave digested in a closed vessel with 8 ml of sulphuric acid, 4 ml of hydrochloric acid and 2 ml of hydrofluoric acid. The times and power of digestion is shown in Table 3.4.

The samples were then made up to a volume of 50 ml in acid washed volumetric flasks with de-ionised water. The solution was then shaken vigorously and allowed to settle in a refrigerator for a minimum of 48 hours to allow all the particles in the solution to settle to the bottom of the flask. The solution was then decanted and analysed for a suite of elements by inductively coupled plasma atomic emission spectrometry (ICP-AES).

3.5.2.2 Anion Analysis

Concentrations of chloride, sulphate and nitrate ions were determined using a Dionex DX100 Ion Chromatograph. One gram of street dust for each size category was added to 50 ml of de-ionised water and stirred continuously for 24 hours. The solutions were then filtered through a series of acid washed glass fibre filter papers prior to analysis.

3.5.2.3 Organic analysis

Dust samples were subjected to the loss on ignition test to determine the percentage of organic matter present (each sample had a weight of approximately 1 g). The samples were oven dried at 105° C for 24 hours, weighed and then heated to 375° C for 16 hours and re-weighed to determine the loss of organic material.

3.5.3 Street dust magnetics analysis

All analyses were based on bulk samples and subjected to the same preparation and analysis procedure described below (Walden *et al.*, 1996).

3.5.3.1 Magnetic susceptibility measurements

A Bartington MS2 magnetic susceptibility meter connected to a Bartington MS2B dual frequency susceptibility sensor was used to make single sample mass specific magnetic susceptibility (χ) measurements. Both low and high frequency susceptibility were measured (χ_{LF} & χ_{HF}), which allowed the frequency dependent susceptibility to be calculated ($\chi_{FD\%}$).

3.5.3.2 Magnetic remanence measurements

Instruments used for remanence included a Molspin alternating field demagnetiser with an anhysteretic remanent magnetisation (ARM) attachment; a Molspin 'small-field' pulse magnetiser; a Molspin 'large-field' pulse magnetiser (0-100 and 0-800 mT); and a Molspin magnetometer connected to a personal computer. The operation and use of each instrument is discussed in detail in Thompson & Oldfield (1986) and Walden *et al.*, (1996).

A Molspin A.F. demagnetiser with a small steady field of 0.04 mT Anhysteretic was used to induce remanence magnetisation. The resultant remanence created within the samples was then measured using a Molspin 1A magnetometer, allowing the calculation of the χ_{ARM}. Following this, the samples were exposed to a demagnetisation field to remove the ARM that had been induced. Samples were then placed into pulse magnetisers and exposed to successively increasing sizes of 'forward' magnetic fields, until a total saturation field of 800 mT was generated. An 800 mT field was chosen in order to represent the Saturation Isothermal Remanent Magnetisation ($SIRM_{800}$ mT), as this was the largest magnetic field the 'large' pulse magnetiser was capable of producing. Applying successively increasing sizes of 'reversed' magnetic fields then destroyed this. After each 'forward' and 'reverse' field, an Isothermal Remanent Magnetisation (IRM) was measured.

3.6 Data analysis

Microsoft Excel 2000 (version 9.0.2720) was used for the majority of data analysis. In this section the analysis techniques used are described. Several of the statistical calculations were checked in SPSS (version 11.5 for Windows), giving identical results each time.

3.6.1 Determining the nature of relationships between two variables

The strength and nature of the relationship between two measured variables was calculated through the use of correlation and regression analysis techniques. The average relationship between two variables is determined by regression analysis, this allows an estimation of the mean value of a dependent variable for any given value of the independent variable. Data were displayed graphically in MS Excel and then a regression line was plotted through the data points. An equation was then calculated which best describes the relationship between the two variables. Linear regression lines were used (least squares regression), unless the plotted data suggested a non-linear relationship between the variables.

Where regression analysis was used to describe the nature of the relationship, the coefficient of determination value (R) was calculated to assess the strength of the relationship between the variables. R can be defined as the proportion of the variance in y attributable to the variance in x. Using the t statistic, the significance of r was tested to

assess the probability of the regression coefficient being derived by chance for a given population size.

In addition to least squares regression, Product Moment Correlation coefficients (*r* value) have also been determined for some data. As with regression, the relationship between the two variables should be roughly linear and follow a straight line and the *t* statistic is then used to determine the probability of the coefficient being determined by chance for a given sample size. The data may be transformed to straighten the plot, but then the correlation calculated would be between the re-expressed variables and not the original ones, so this has been avoided.

3.6.2 Detecting significant differences between two or more sample means

When it was necessary to determine whether two sample means were statistically different, a *t*-test was used. However, it is not valid to use a *t*-test for the comparison of several sample means, so in this case ANOVA (Analysis of Variance) is used. The major assumption with ANOVA is that the variance of the samples being tested is equal. If this is not the case transformation of the data may be required.

Chapter 4

Results

4.1 Introduction

The results presented in the following chapter can be divided into three relatively distinct areas, namely, airborne particulate measurements, settled dust analysis and street dust analysis. However, the results within the three main areas of research are largely inter-related and clear boundaries between data yielded by experiments are difficult to define. For the sake of clarity, the results within each section have been divided into sections where important elements of the research can be presented.

4.2 Relationships between indoor and outdoor airborne particulate matter and seasonality

Indoor and outdoor measurements of respirable particulate matter were taken on a daily basis between September 2000 and August 2001 for Building One. After the removal of anomalous results, such as negative weight loadings (likely to be a consequence of static charge) or very high out of the ordinary readings (possibly due to error in the initial weighing), the sampling yielded 143 pairs of measurements within one year.

A regression analysis for all the samples gives an R^2 value of 0.551 ($n = 143, p < 0.01, f$ ratio = 61.32) (Figure 4.1), shows that a significant relationship exists, suggesting that indoor concentrations of respirable particulate matter are closely related to outdoor

concentrations. This is further supported by many of the larger outdoor peaks in particulate matter concentrations being reflected indoors (Figure 4.2).

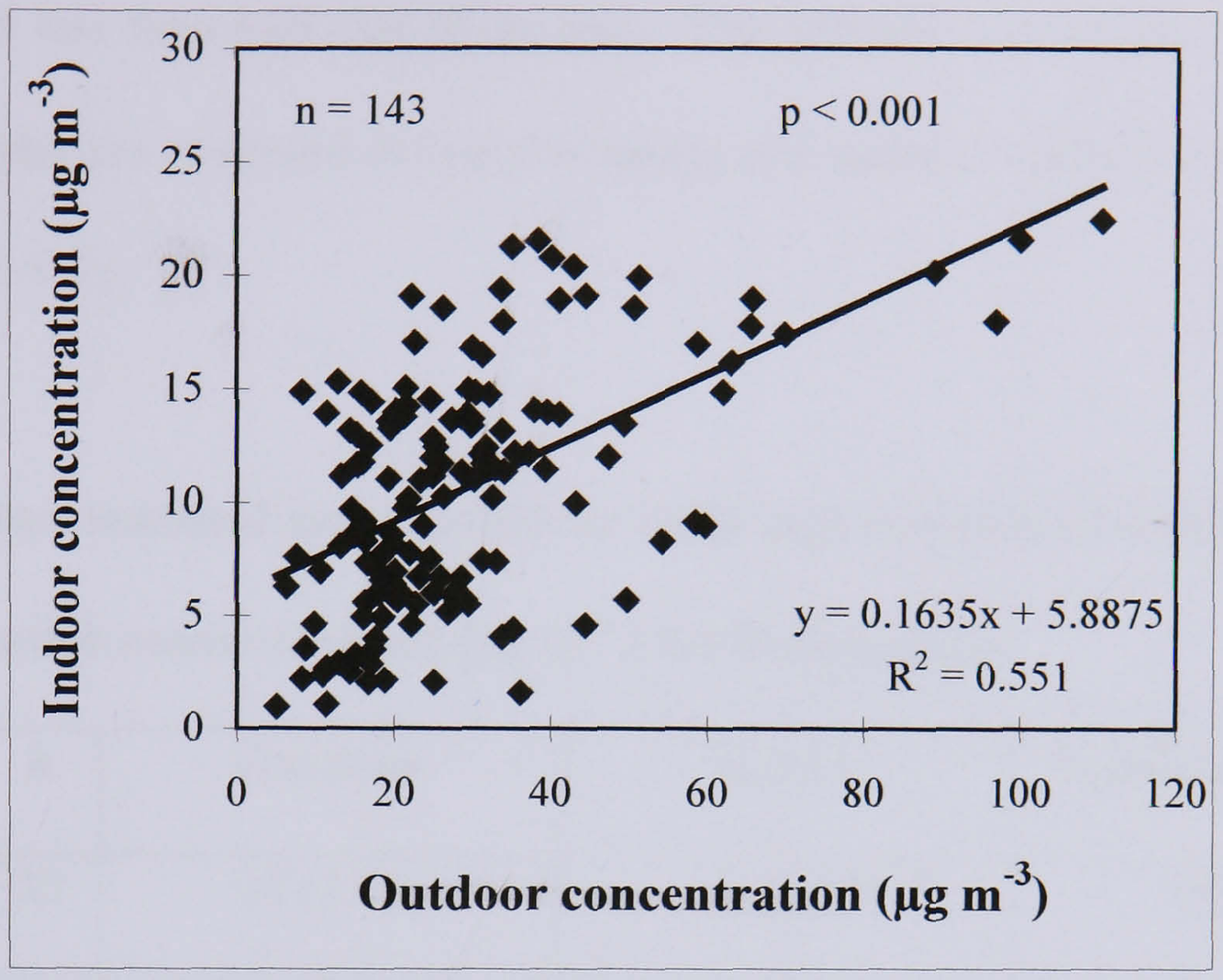


Figure 4.1: Regression analysis between indoor and outdoor respirable particulate matter concentrations for Building One

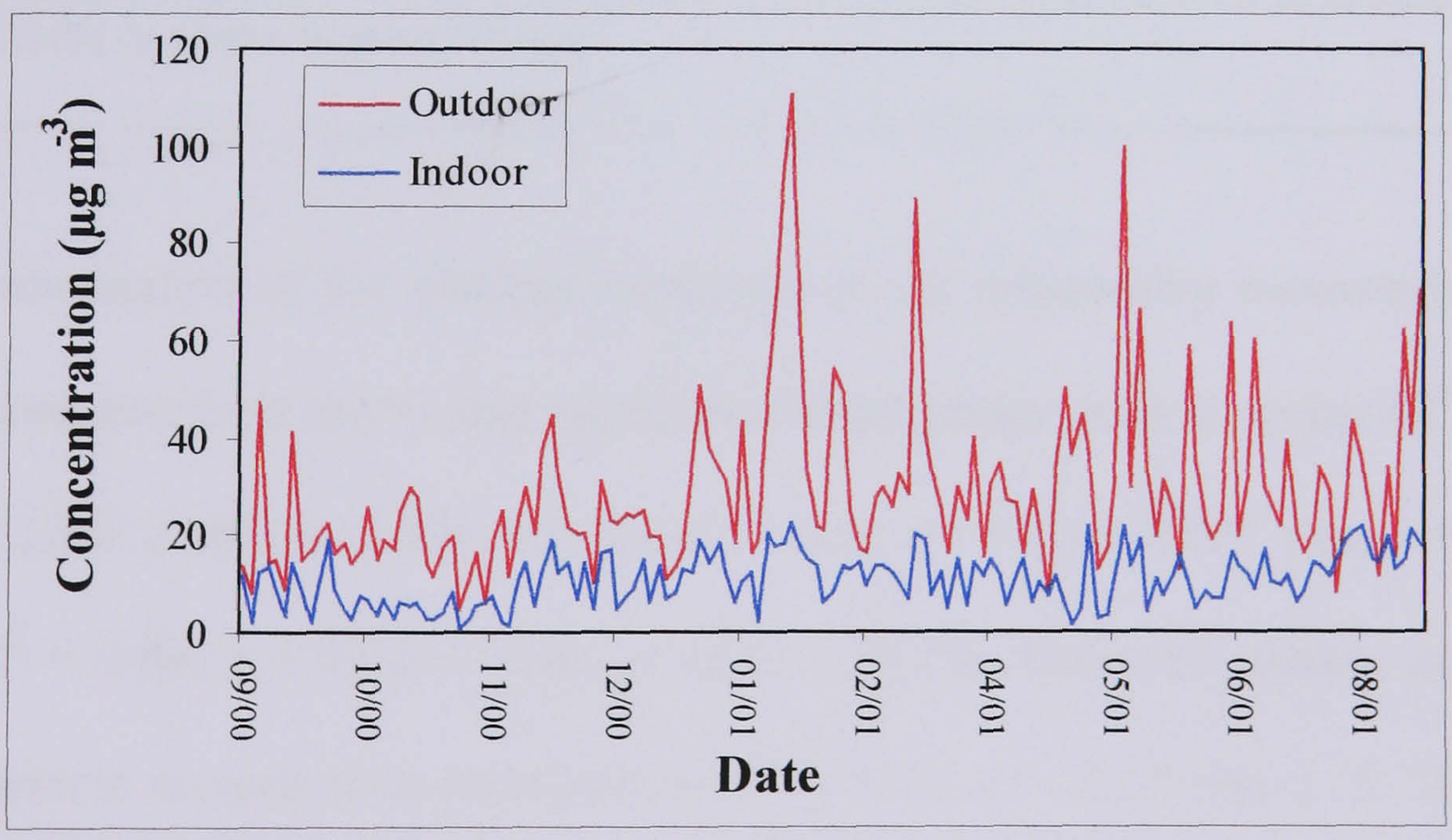


Figure 4.2: Seasonal variation in indoor and outdoor respirable particulate matter for Building One

A mean indoor:outdoor ratio of 0.42 (SE = 0.02) also suggests there is no significant indoor source of particulate matter. When the results are broken down into seasons it is clear that the indoor:outdoor ratio in summer is highest (0.51), with winter (0.19) being the lowest and less than half that of summer. The greatest concentrations of respirable particulate matter are observed during the spring and summer months, both indoors and outdoor (Table 4.1).

Table 4.1: Mean seasonal indoor:outdoor ratio and indoor and outdoor respirable particulate matter concentrations (μg m^{-3}) for Building one

Season	*n*	Outdoor	Indoor	Indoor:outdoor ratio
Spring	30	34 (3.72)	11 (1.12)	0.36 (0.04)
Summer	33	30 (2.47)	12 (0.88)	0.51 (0.06)
Autumn	33	20 (1.54)	8 (0.77)	0.39 (0.06)
Winter	35	22 (3.77)	5 (0.86)	0.19 (0.03)
Standard error is show in parenthesis				

Further examination of the seasonal variations in the relationship between indoor and outdoor concentrations shows that significant relationships exist in spring ($R^2 = 0.58$, $n = 30$, $p < 0.001$, f ratio = 13.89), autumn ($R^2 = 0.62$, $n = 33$, $p < 0.001$, f ratio = 0.55) and winter ($R^2 = 0.64$, $n = 35$, $p < 0.001$, f ratio = 26.79). However, during the summer months there is no noticeable relationship ($R^2 = 0.13$, $n = 33$, f ratio = 22.37) (Figures 4.3 to 4.6).

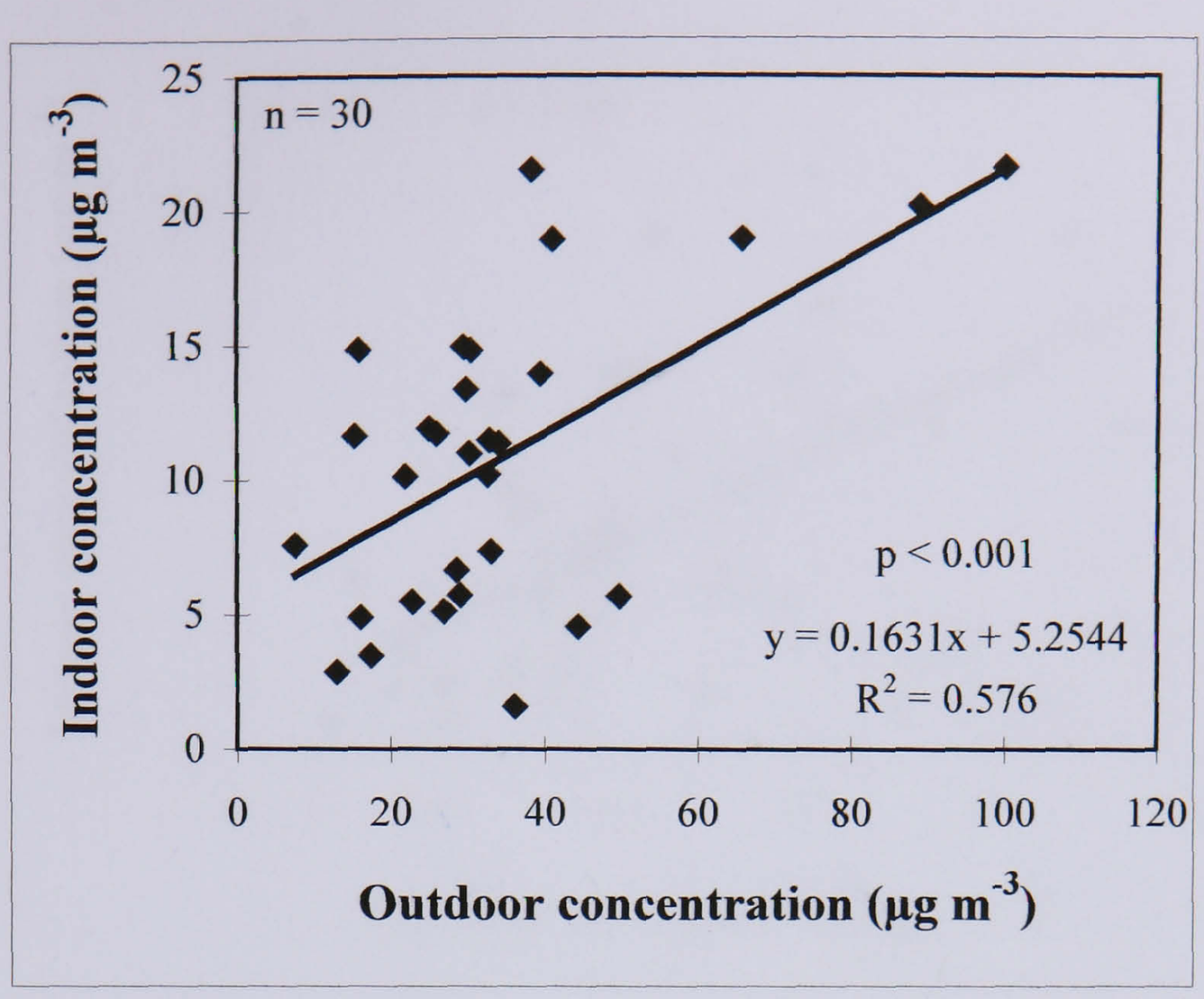


Figure 4.3: Regression analysis between indoor and outdoor respirable particulate concentrations measured in spring for Building One

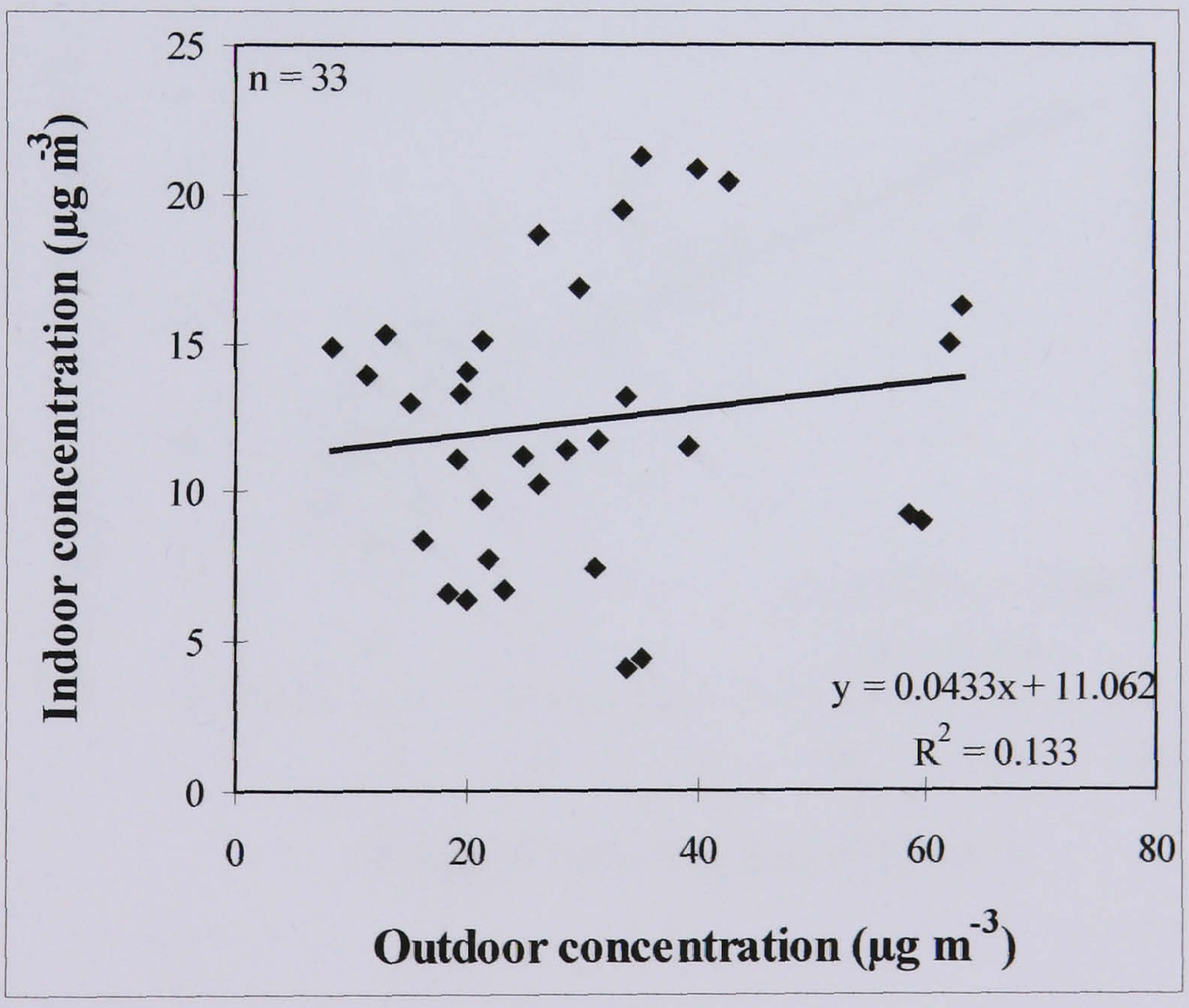


Figure 4.4: Regression analysis between indoor and outdoor respirable particulate concentrations measured in summer for Building One

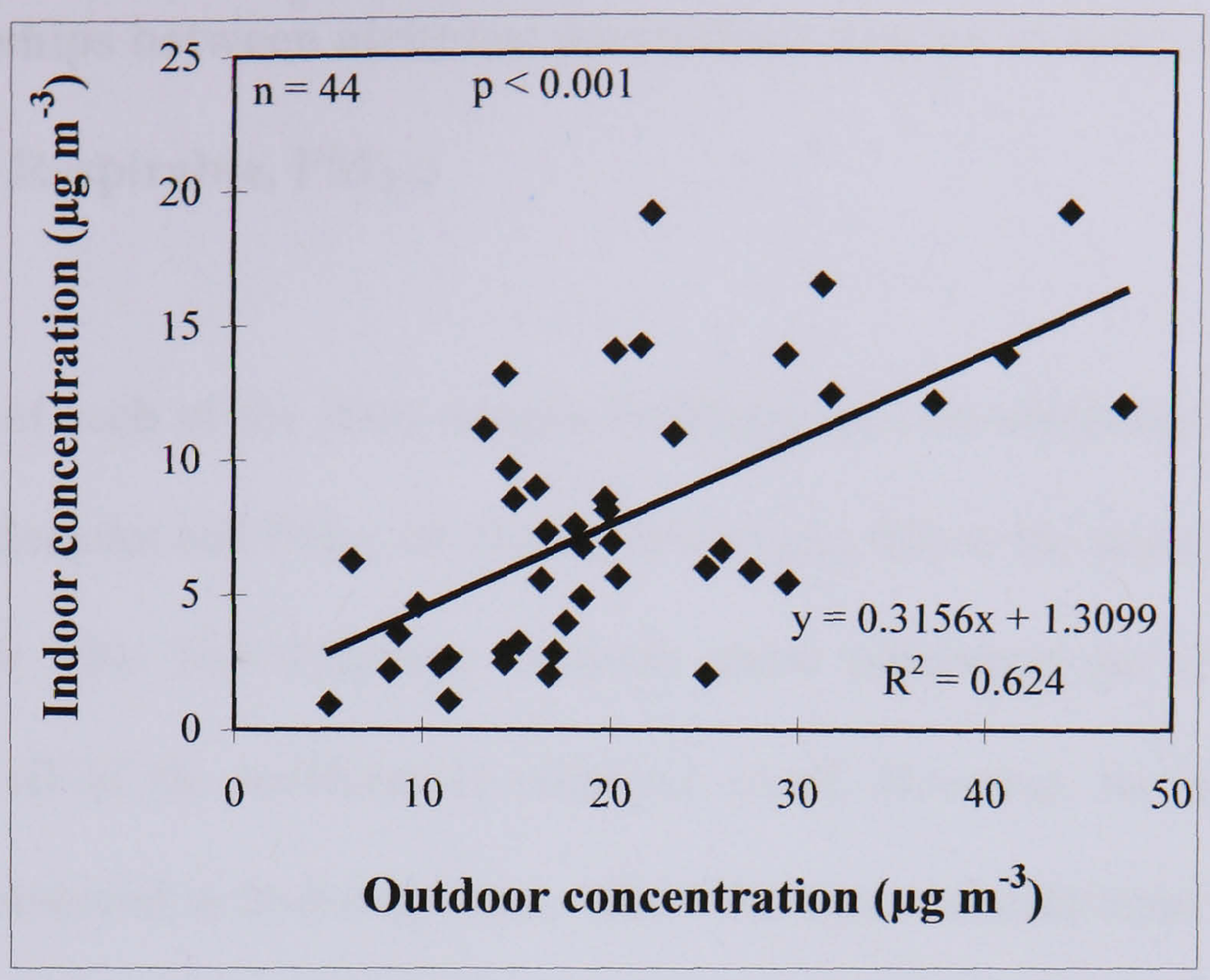


Figure 4.5: Regression analysis between indoor and outdoor respirable particulate concentrations measured in autumn for Building One

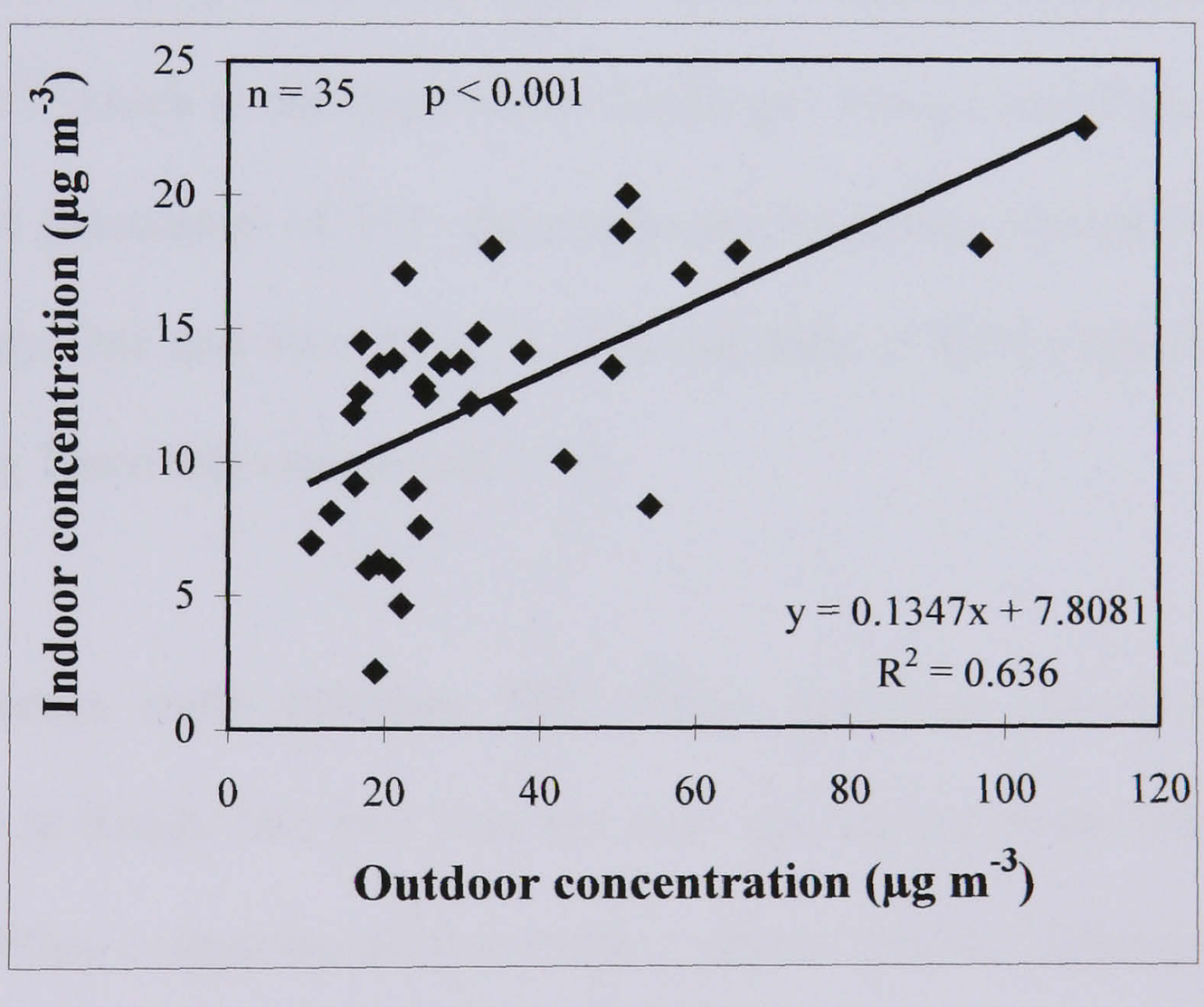


Figure 4.6: Regression analysis between indoor and outdoor respirable particulate concentrations measured in winter for Building One

4.3 Relationships between airborne particulate matter of different diameters (TSP, PM_{10}, Respirable, $PM_{2.5}$)

In the foyers of each of the three sample buildings the concentrations of TSP, PM_{10}, respirable particulates and $PM_{2.5}$ are closely related and follow the same trend over time (Figure 4.7 to 4.9). The difference between mean concentrations of the four size categories in all of the buildings is relatively small. However, the most noticeable difference is observed in Building Three, where the mean concentration of TSP is 14.5 $\mu g\ m^{-3}$ and the mean concentration of $PM_{2.5}$ is 10.6 $\mu g\ m^{-3}$, giving a significant difference of 3.9 $\mu g\ m^{-3}$ ($n = 30$, $p < 0.05$). A similar difference is also seen in Building Two with a significant difference of 3.2 $\mu g\ m^{-3}$ being measured between TSP and $PM_{2.5}$ concentrations ($n = 30$, $p < 0.05$). In contrast, in Building One the difference is smaller at just 1 $\mu g\ m^{-3}$, which is not statistically significant. $PM_{2.5}$ concentrations can also be expressed as a percentage of TSP concentrations to further illustrate this difference. Inside Buildings One and Two $PM_{2.5}$ is 91% and 80% of TSP, respectively, however, inside Building Three this value is just 73%.

For measurements made outdoors TSP, PM_{10}, respirable particulates and $PM_{2.5}$ concentrations at Roads One and Two are also very closely related (Figure 4.10 and Figure 4.11). When comparing the two roads it appears that the differences between the concentrations of TSP and $PM_{2.5}$ is similar, with the differences between TSP and $PM_{2.5}$ being 7.72 $\mu g\ m^{-3}$ and 7.52 $\mu g\ m^{-3}$ for Road One and Road Two, respectively. However,

when $PM_{2.5}$ is expressed as a percentage of TSP, the difference is clear with $PM_{2.5}$ accounting for 69% of TSP at Road One and 59% at Road Two.

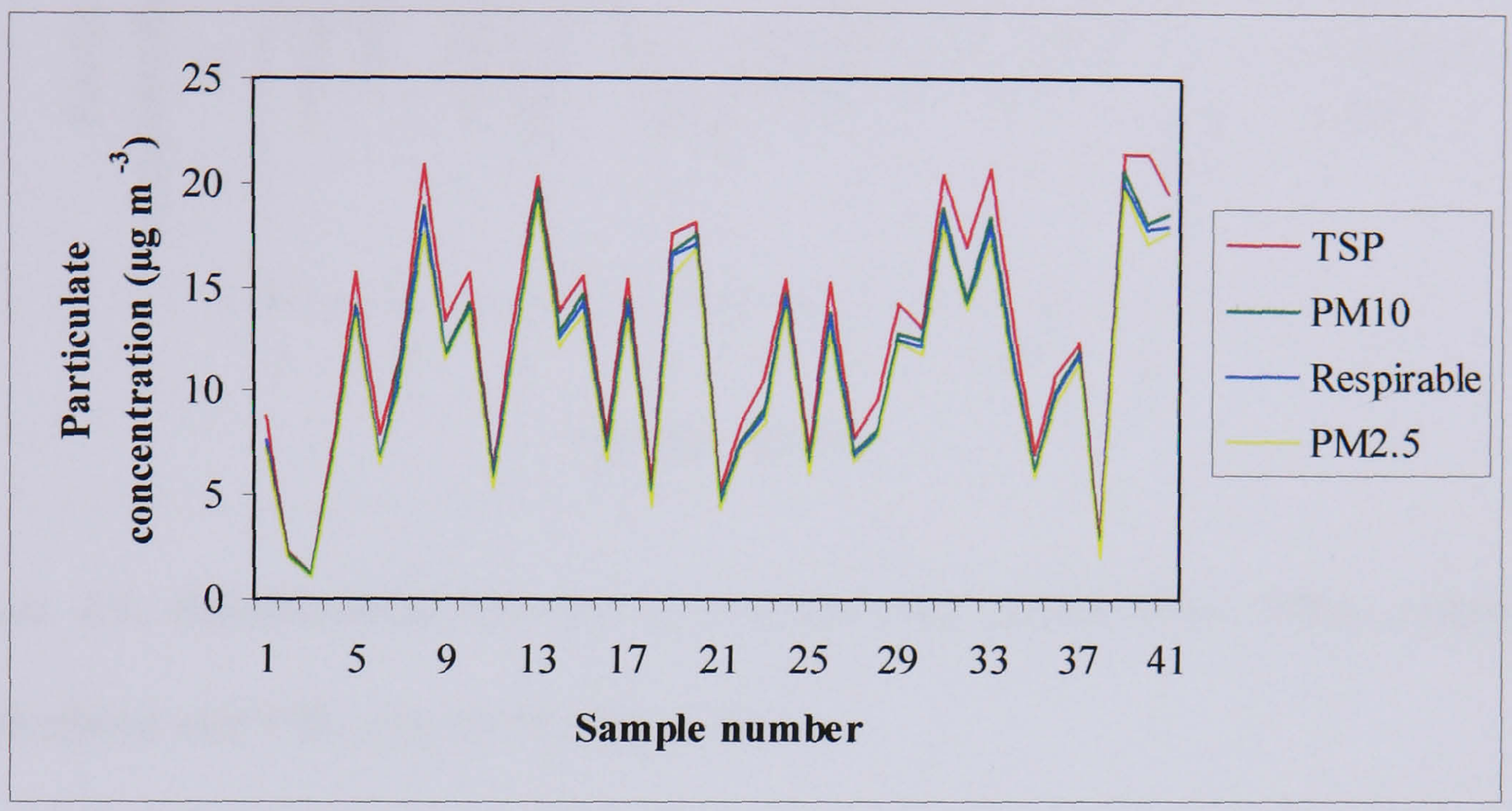


Figure 4.7: Relationship between total suspended particulates, PM_{10}, respirable particulates and $PM_{2.5}$ inside Building One

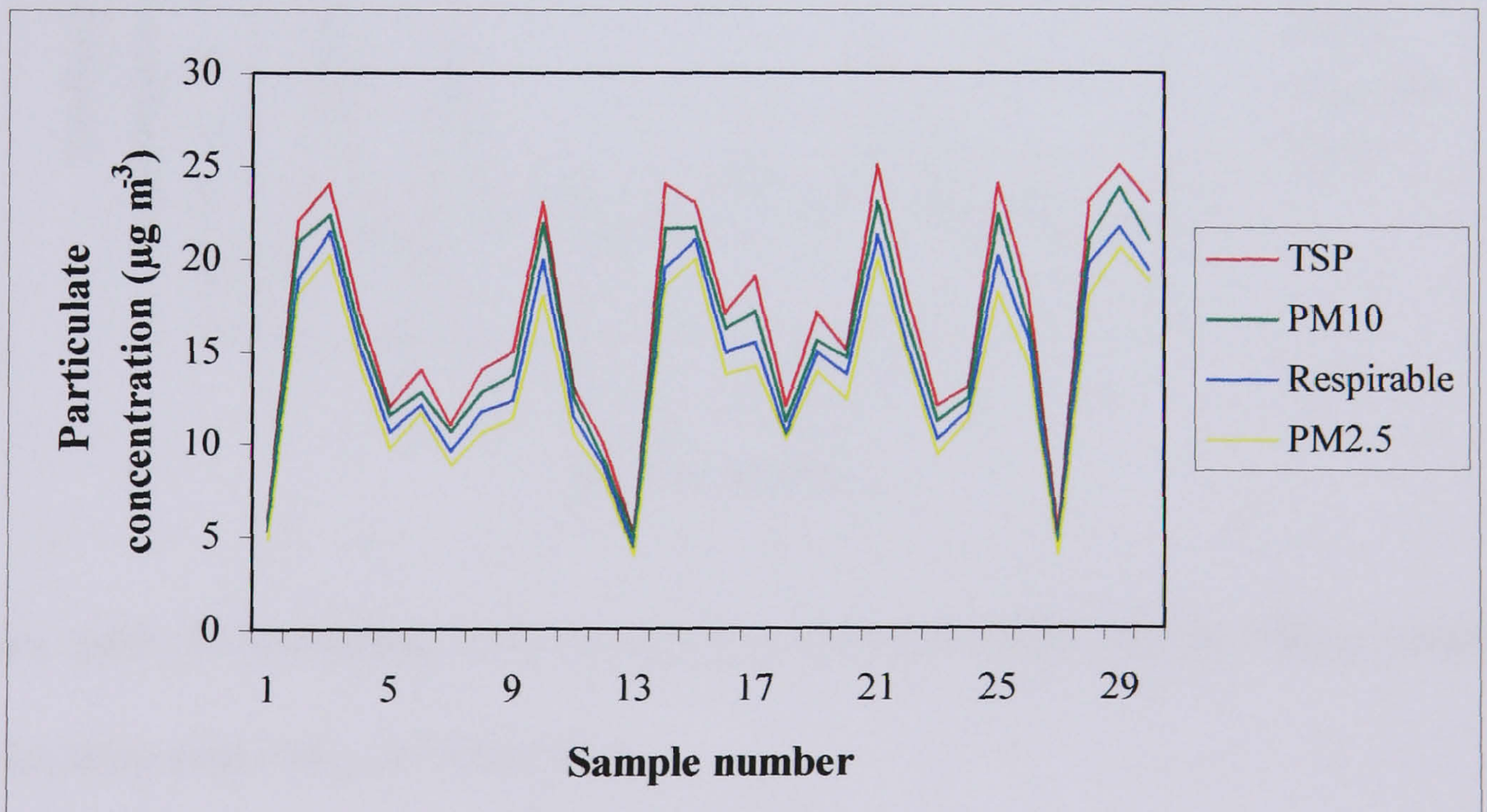


Figure 4.8: Relationship between total suspended particulates, PM_{10}, respirable particulates and $PM_{2.5}$ inside Building Two

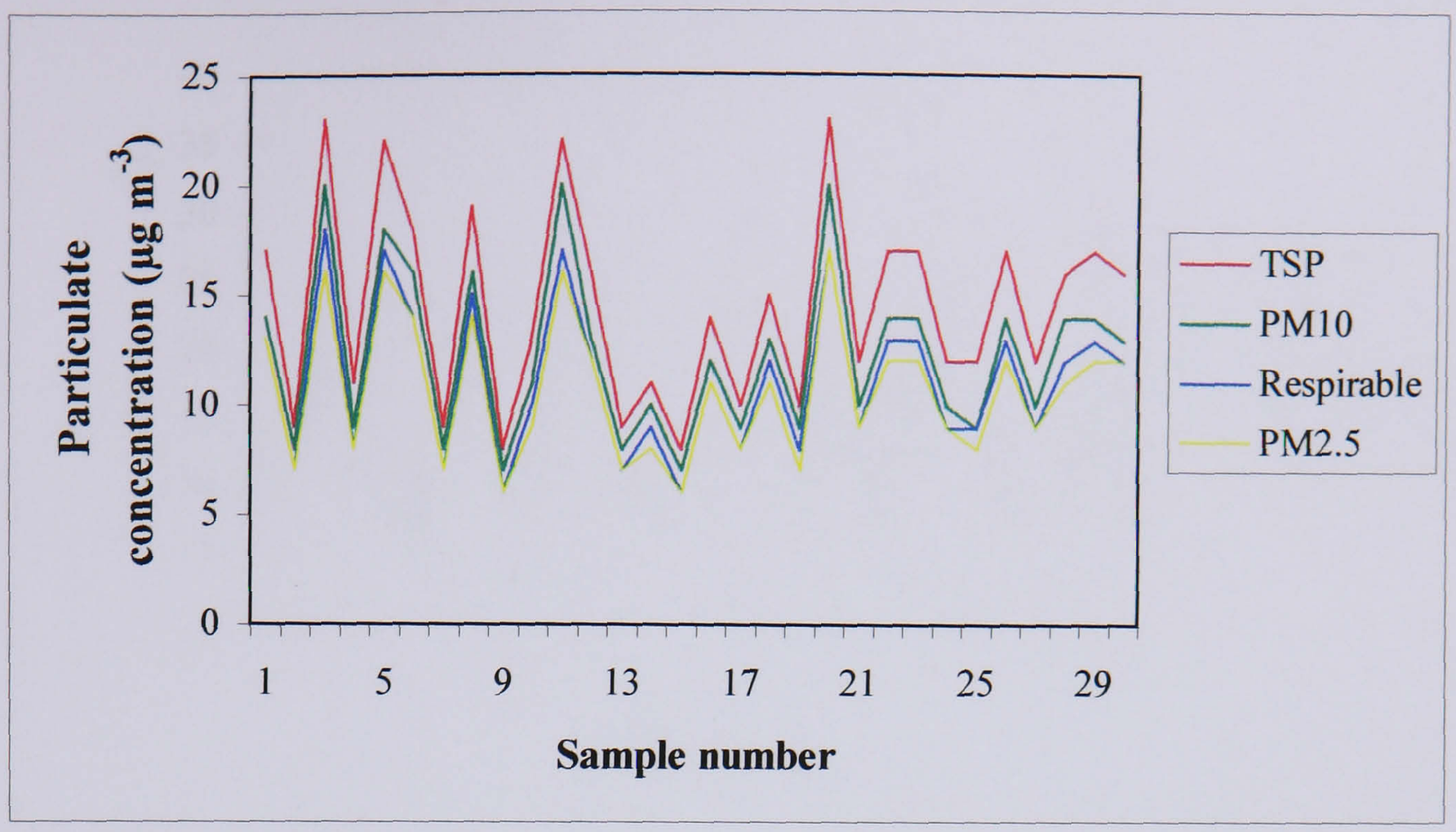


Figure 4.9: Relationship between total suspended particulates, PM_{10}, respirable particulates and $PM_{2.5}$ inside Building Three

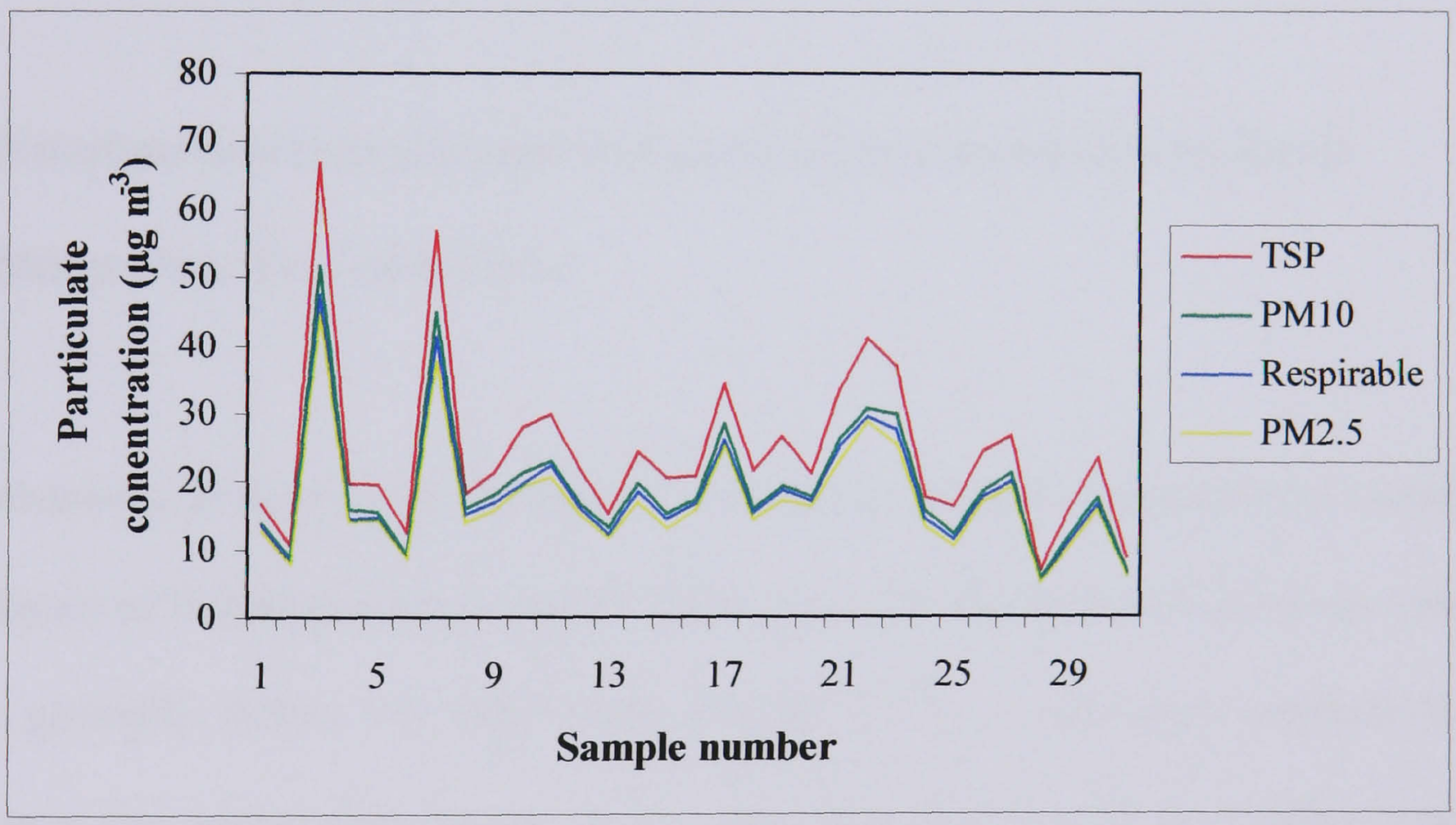


Figure 4.10: Relationship between total suspended particulates, PM_{10}, respirable particulates and $PM_{2.5}$ at Road One

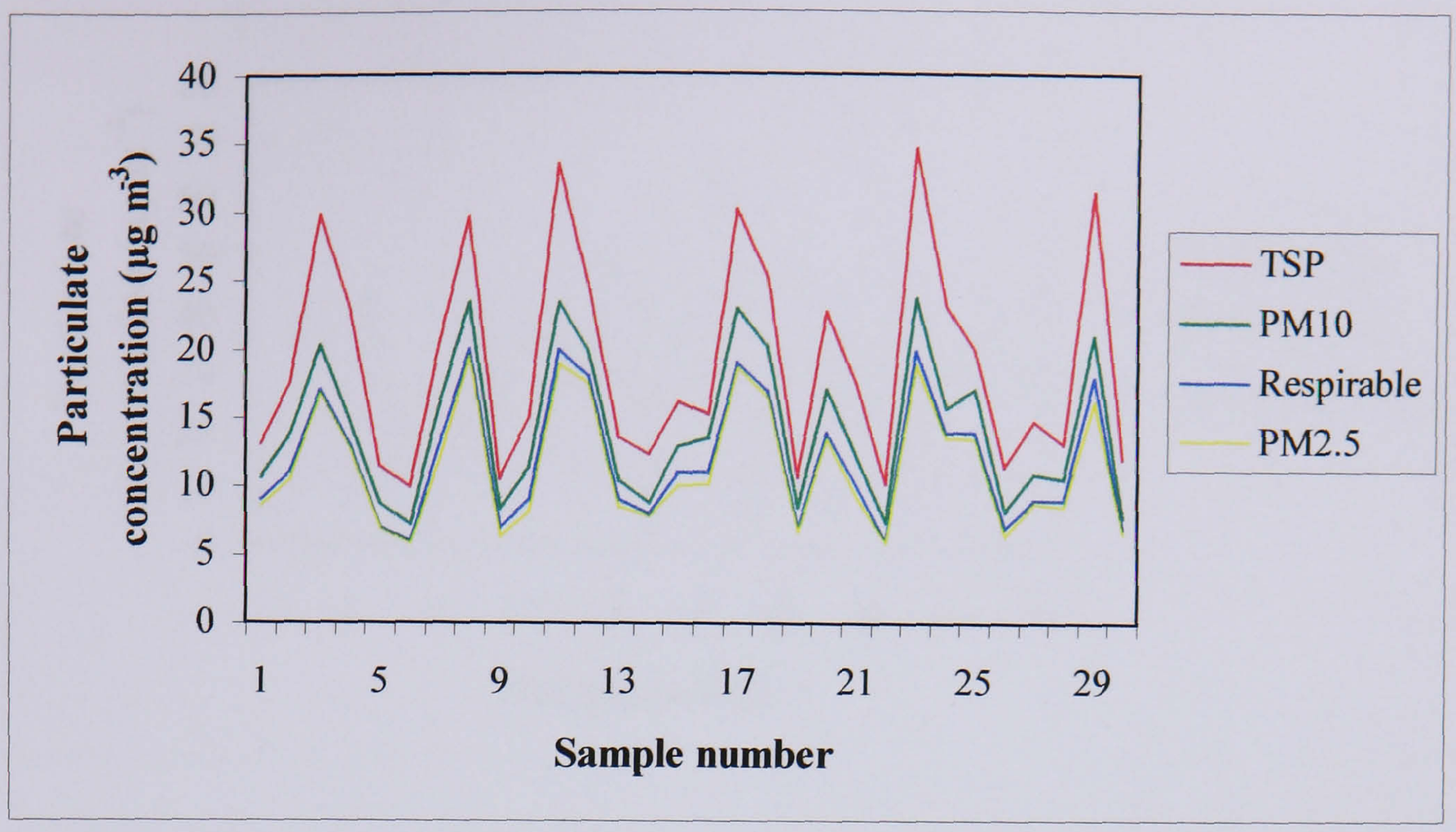


Figure 4.11: Relationship between total suspended particulates, PM_{10}, respirable particulates and $PM_{2.5}$ at Road Two

4.4 Simultaneous measurements of particulate concentrations inside Buildings One, Two and Three

Simultaneous 24 hour measurements of respirable particulate concentrations recorded in the foyers of Buildings One, Two and Three show that levels inside Buildings One and Two generally follow the same trend (Figure 4.12). A regression analysis further indicates this relationship, giving an R^2 value of 0.785 (n = 37, $p < 0.001$, f ratio = 56.17) (Figure 4.13). It is also clear that the three buildings contain different concentrations of respirable particulate matter. Over the sample period the mean concentrations for the three buildings were 20.4 µg m^{-3} (SE = 2.28) for Building One, 32.2 µg m^{-3} (SE = 2.87) for Building Two, 10.1 µg m^{-3} (SE = 1.93) for Building Three. ANOVA analysis shows these differences to be significant ($p < 0.01$).

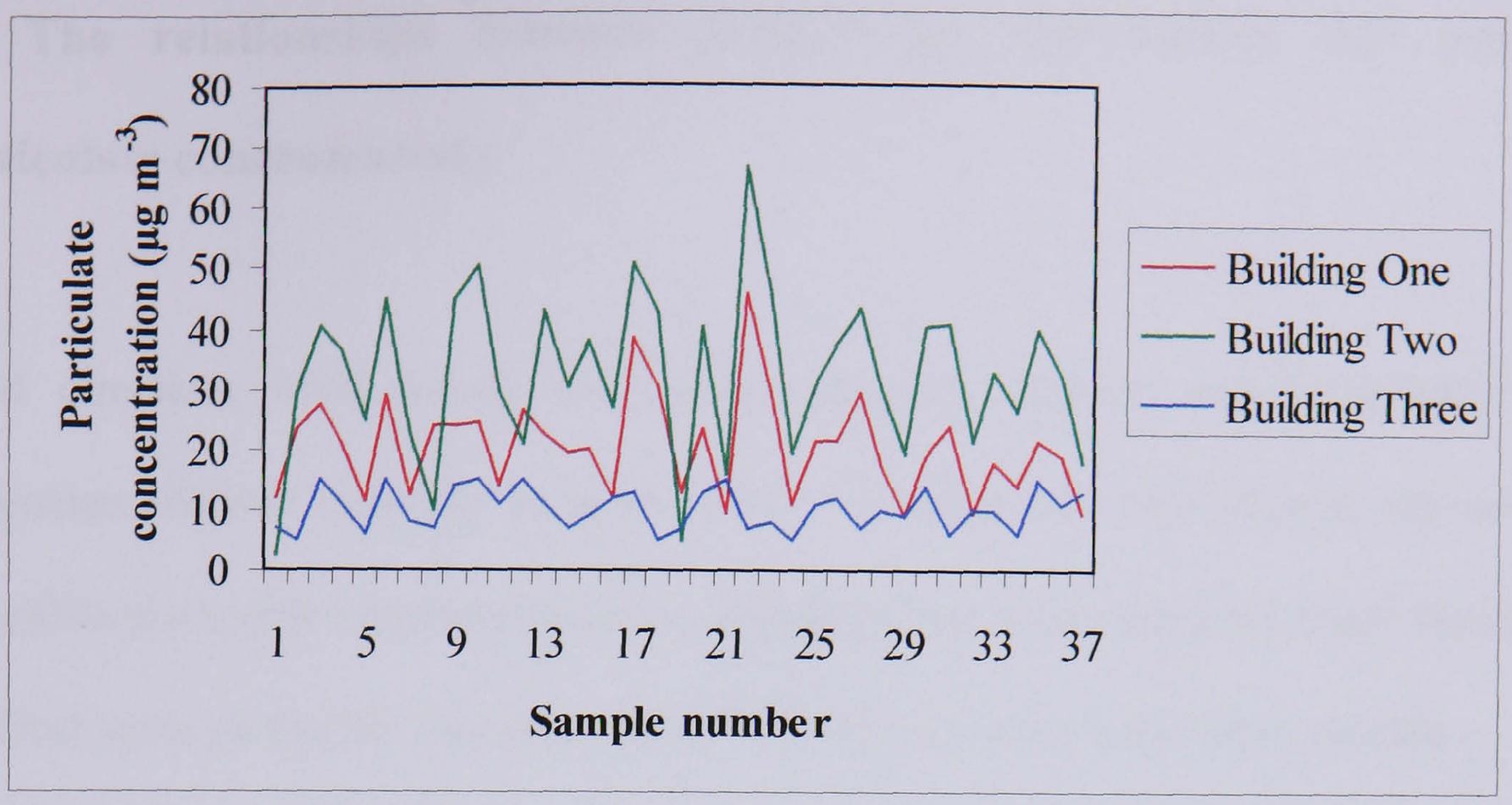


Figure 4.12: Comparison between respirable particulate concentrations in the foyers of buildings One, Two and Three

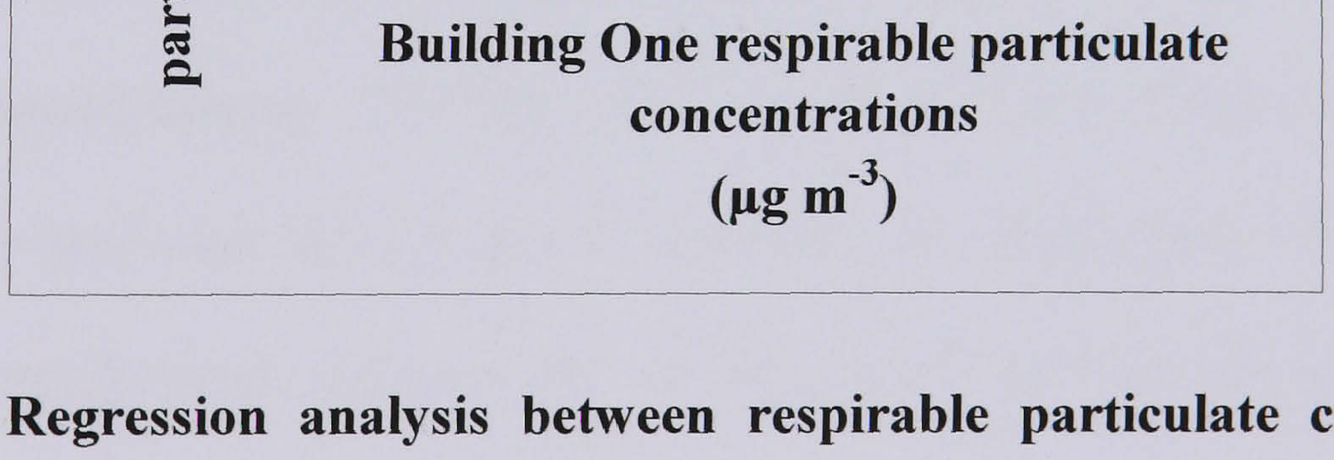


Figure 4.13: Regression analysis between respirable particulate concentrations inside the foyers of Buildings One and Two

4.5 The relationships between meteorology and indoor and outdoor particulate concentrations

Wind direction, wind speed, atmospheric pressure, rainfall duration/quantity and percentage relative humidity were recorded simultaneously with indoor and outdoor respirable particulate concentrations for Building One. Each meteorological factor and its effect upon particulate concentrations are displayed in the appropriate section.

4.5.1 Wind direction

A distinct relationship has been observed between wind direction, indoor respirable particulate concentrations and outdoor concentrations measured for Building One (Figure 4.14 to 4.16). It is clear that both indoor respirable particulate concentrations are greater when the wind is coming from a northerly and to a lesser extent southerly direction, this being perpendicular to the street canyon. When the wind direction is generally eastward or westward, therefore parallel to the canyon, particulate concentrations show a noticeable decline, with concentrations being lowest when wind direction is approximately 112° and 270° east from north (Figure 4.14). Outdoor concentrations have also been observed following this relationship. There is a much smaller difference between northerly and southerly wind directions, however, the lowest concentrations are still observed with wind at approximately 112° and 270° east from north (Figure 4.15). Indoor:outdoor ratio also follows a similar pattern with a greater indoor:outdoor ratio observed during perpendicular wind directions. Similarly,

indoor:outdoor ratio when wind direction is approximately 112° and 270° east from north is very low (Figure 4.16). The effect of wind direction upon indoor:outdoor ratio and particulate concentrations is summarised in Figures 4.17 and 4.18.

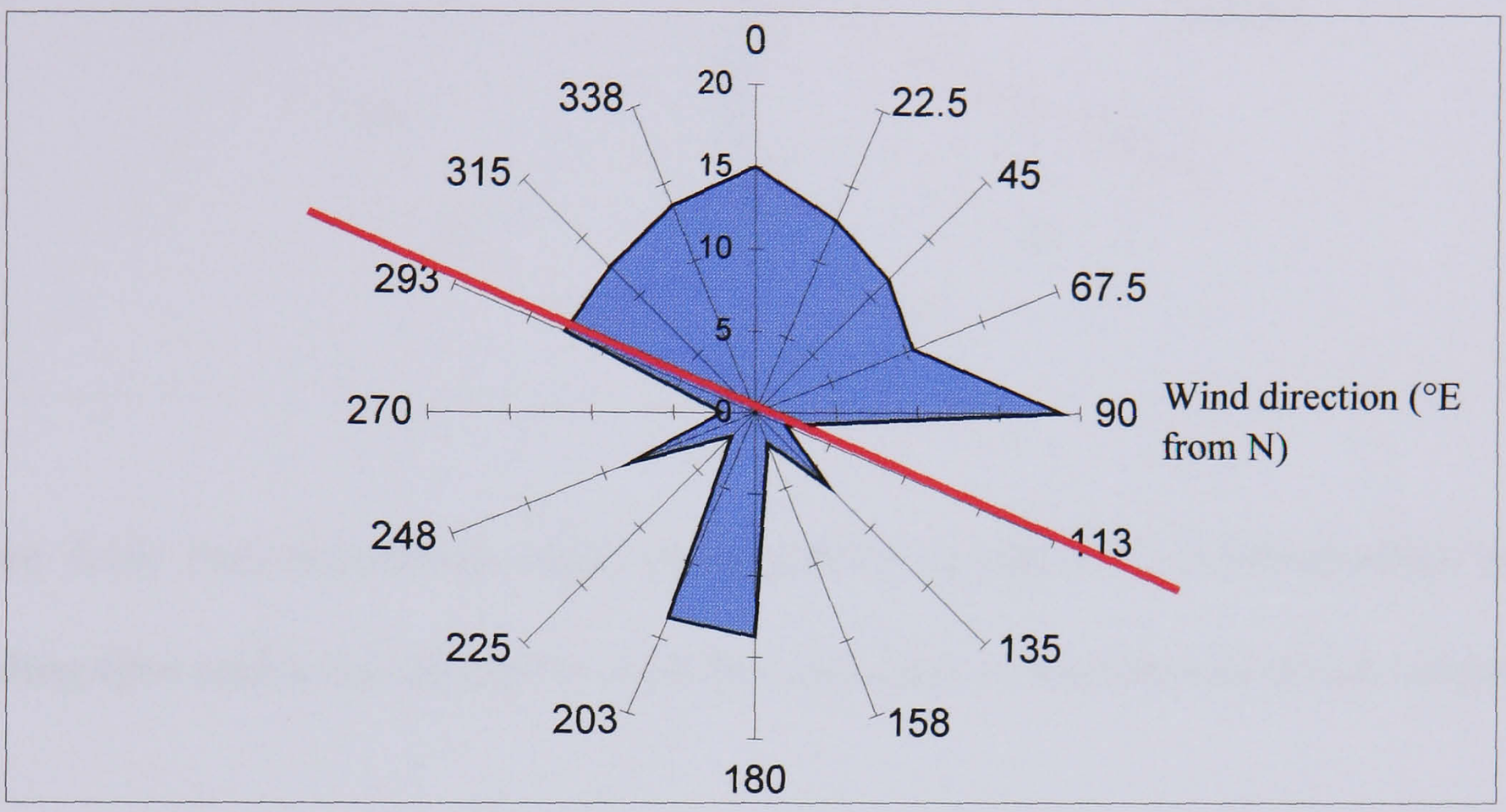


Figure 4.14: Indoor respirable particulate concentration (µg m^{-3}) inside Building One and wind direction (red line indicates orientation of street canyon)

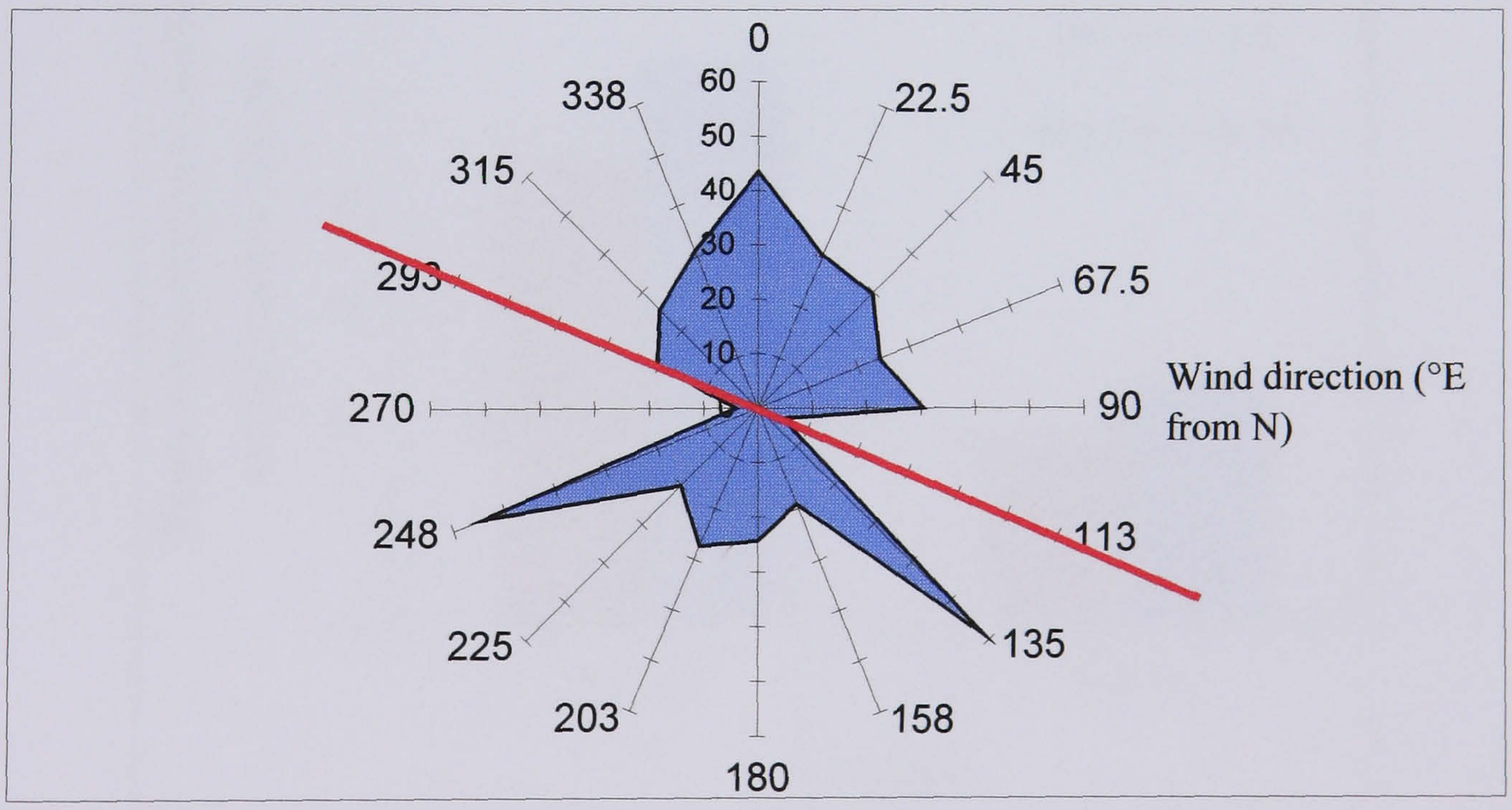


Figure 4.15: Outdoor respirable particulate concentration (µg m^{-3}) inside Building One and wind direction (red line indicates orientation of street canyon)

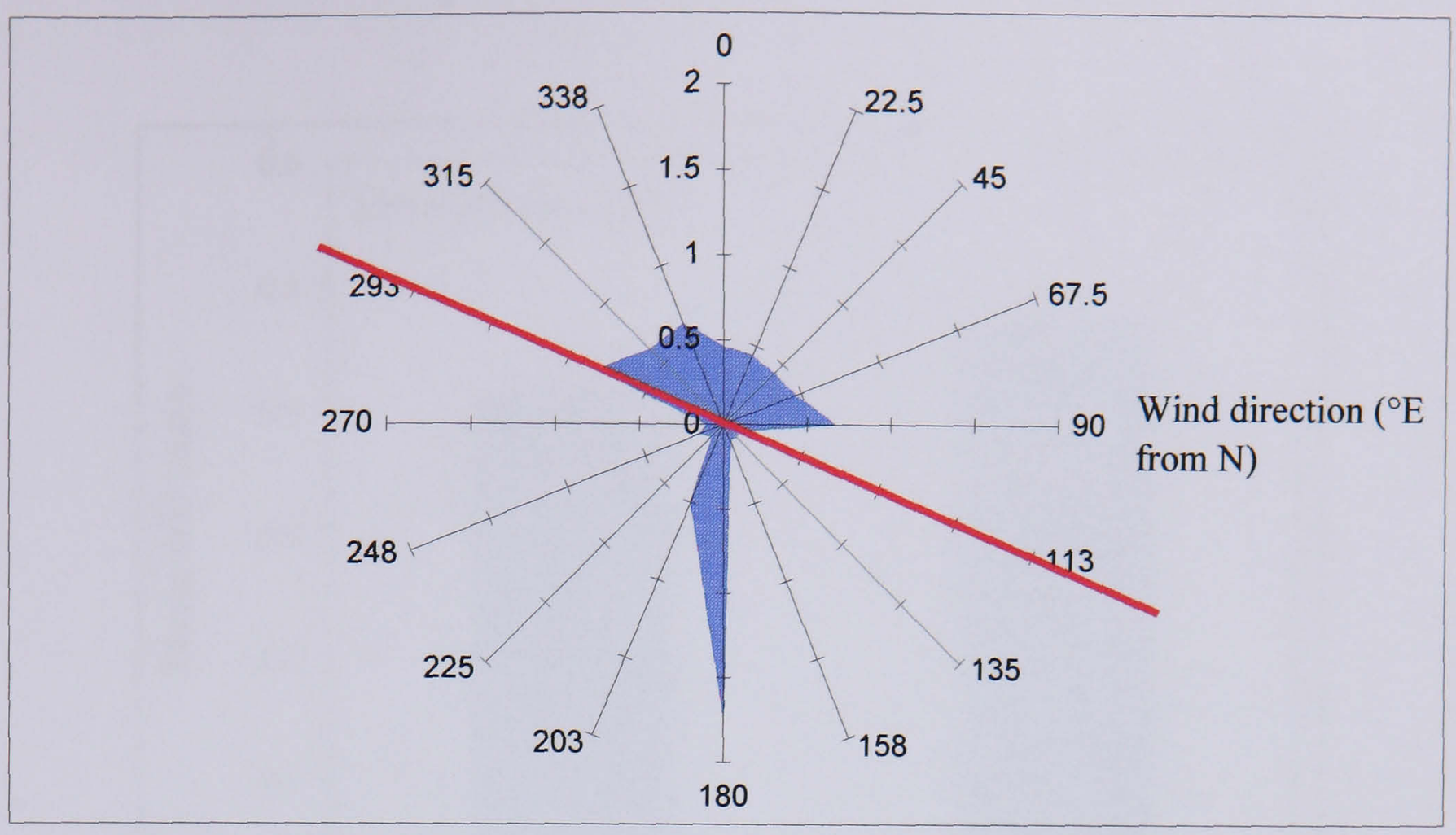


Figure 4.16: Indoor:outdoor ratio of respirable particulate concentration inside Building One and wind direction (red line indicates orientation of street canyon)

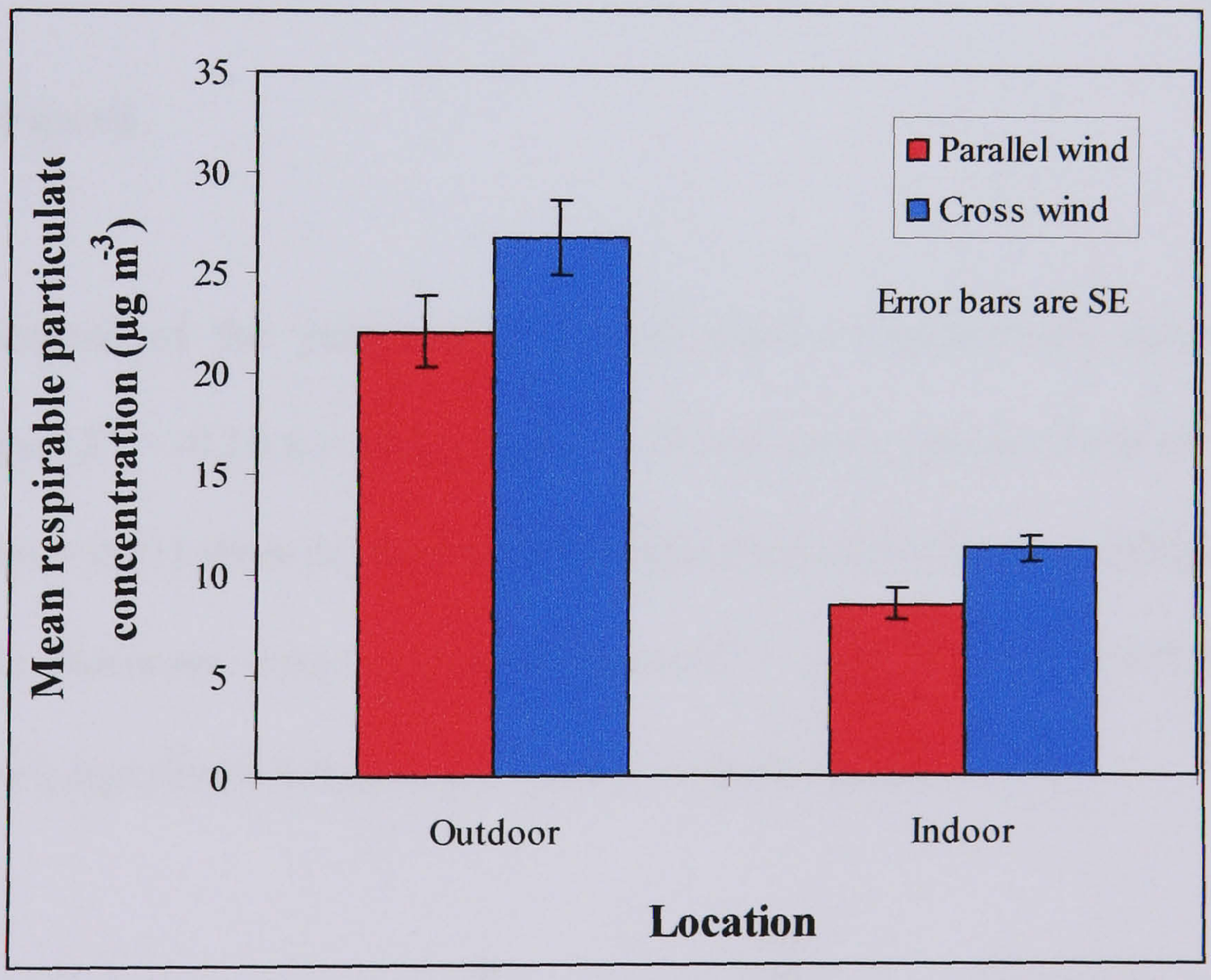


Figure 4.17: The effect of wind direction on mean outdoor and mean indoor respirable particulate concentrations

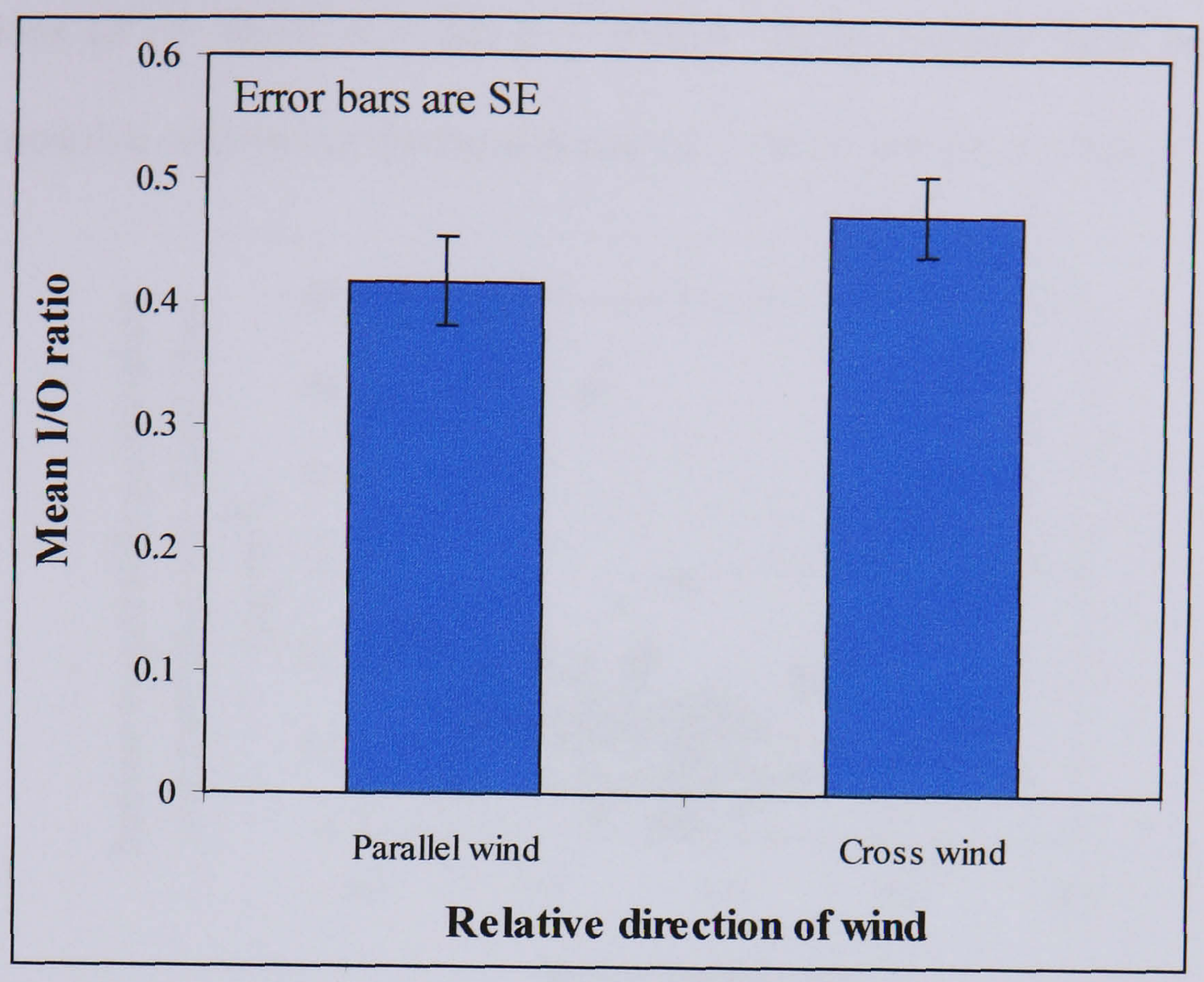


Figure 4.18: The effect of wind direction on mean indoor:outdoor ratio

4.5.2 Wind speed

Over the course of the year respirable particulate concentrations measured inside Building One (R^2 = -0.18 n = 131, f ratio = 4.3) and indoor:outdoor ratio (R^2 = -0.006, n = 117, f ratio = 0.01) show no discernable relationship with wind speed (Figure 4.19 and Figure 4.20). However, outdoor concentrations (R^2 = -0.35, n = 119, $p < 0.001$, f ratio = 13.01) show a significant negative correlation (Figure 4.21).

When the results are broken down into seasons the observed relationships become more complex, with a distinct seasonal variation in correlations observed (Table 4.2). Significant negative correlations are only observed during winter months for outdoor

measurements (R^2 = -0.54, n = 30, p < 0.001) and during summer for indoor concentrations (R^2 = -0.41, n = 35, p < 0.001). Indoor:outdoor ratio only shows a significant positive correlation during summer (R^2 = 0.33, n = 27, p < 0.01).

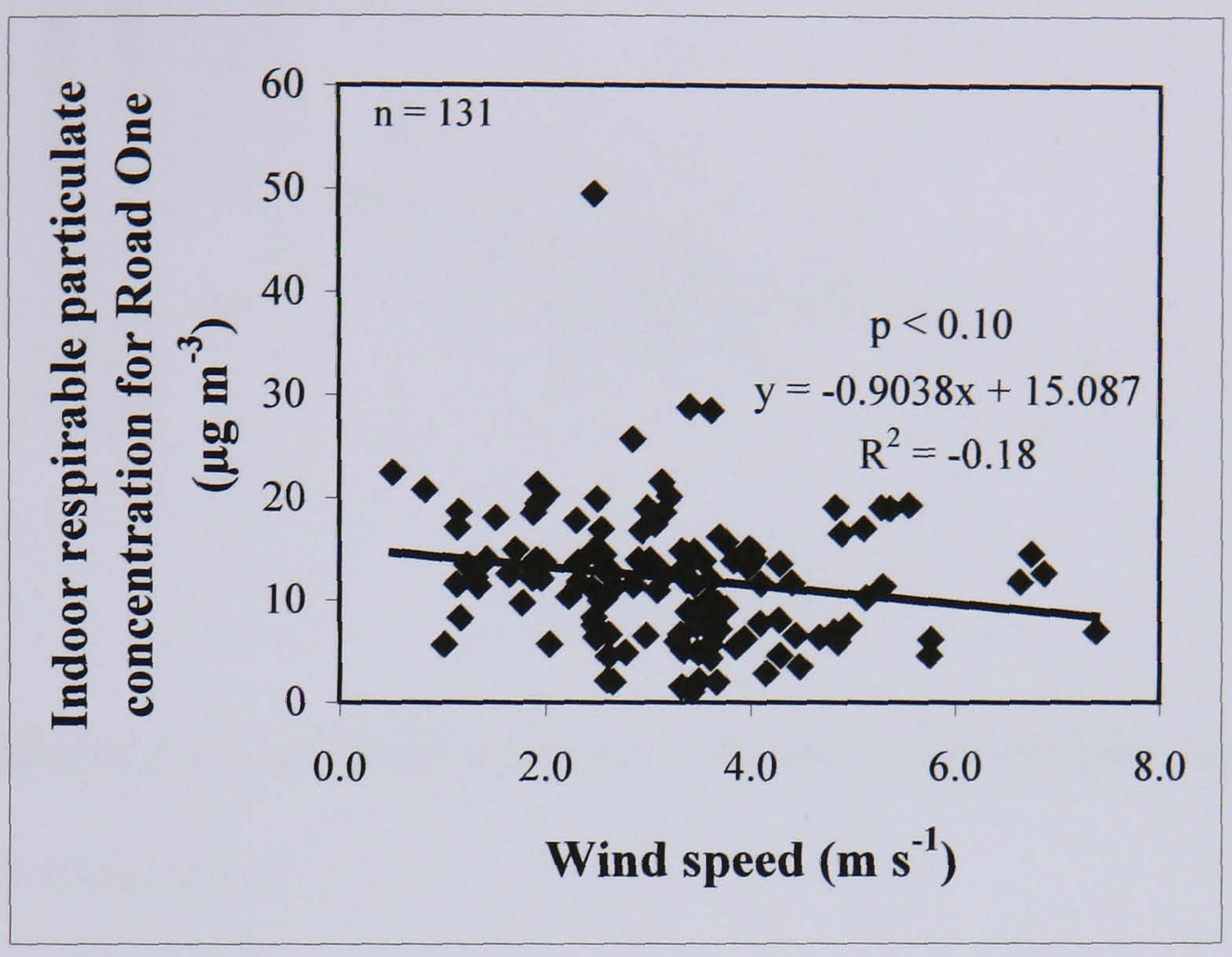


Figure 4.19: Regression analysis between respirable particulate concentration inside Building One and wind speed

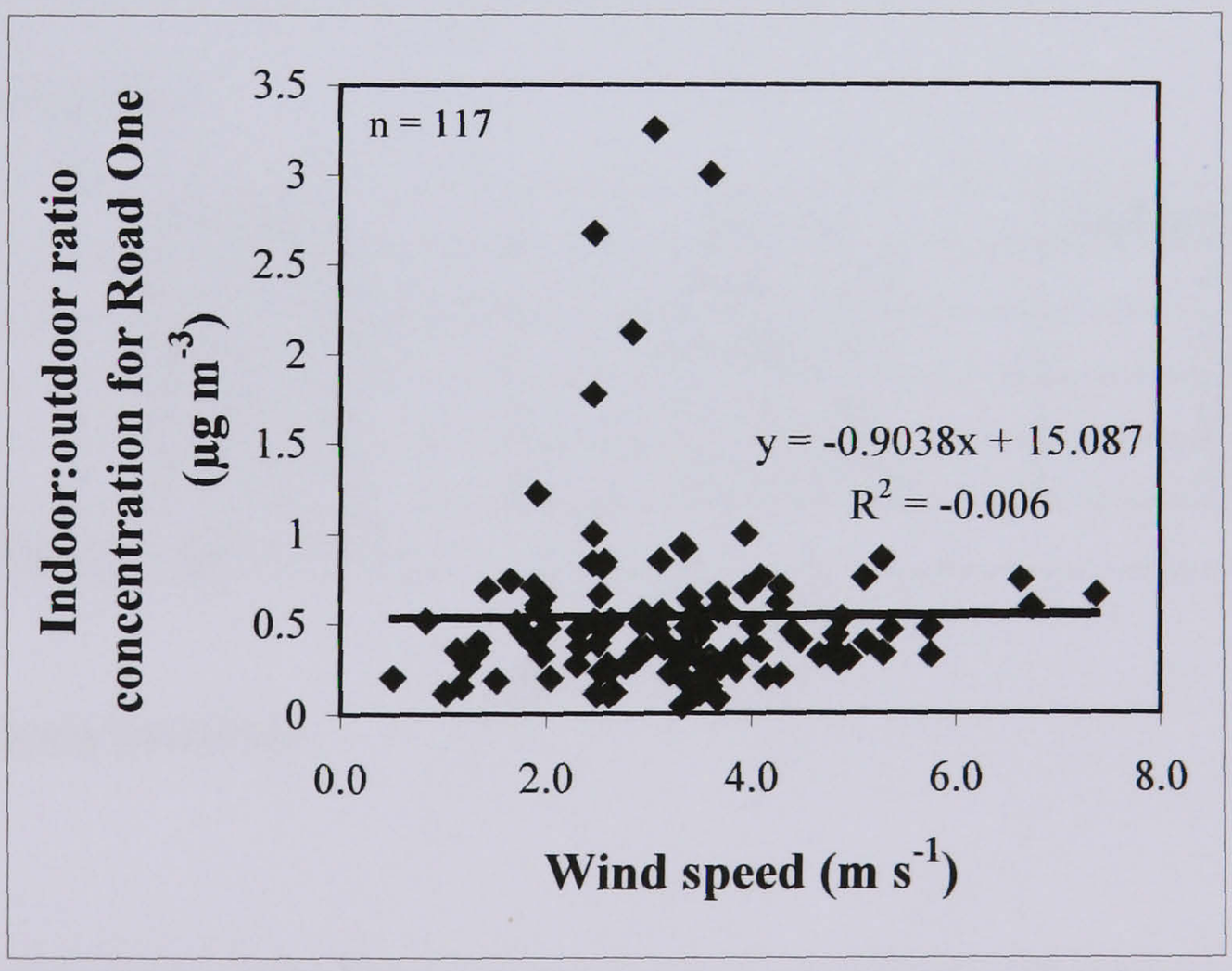


Figure 4.20: Regression analysis between indoor:outdoor ratio of respirable particulate concentrations for Building One and wind speed

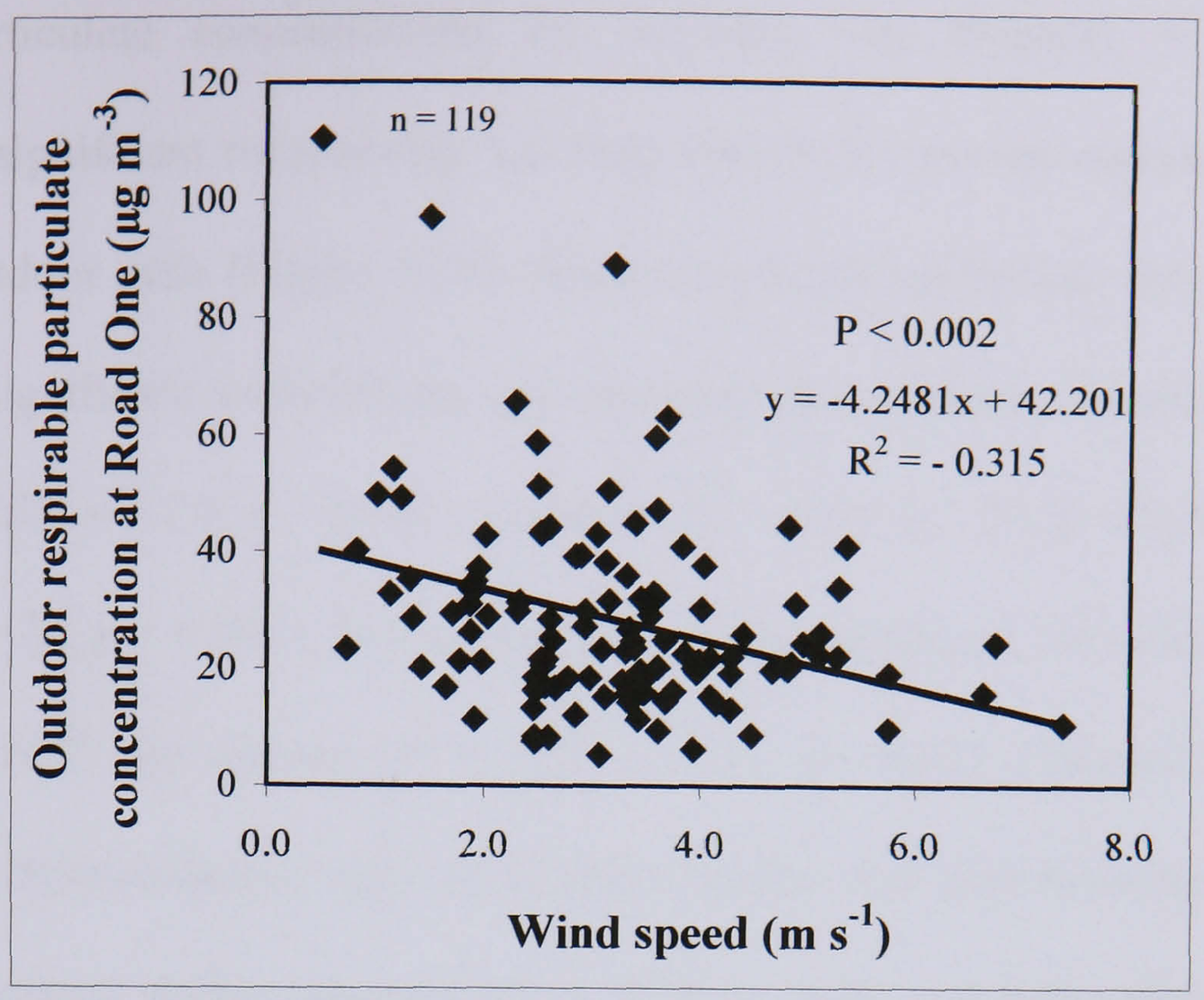


Figure 4.21: Regression analysis between respirable particulate concentration at Road One and wind speed

Table 4.2: Correlation matrix for wind speed and indoor respirable particulate concentration, outdoor respirable particulate concentration and indoor:outdoor ratio for Building One

	Outdoor	Indoor	Indoor:outdoor ratio
Spring	-0.070 (24)	-0.041 (35)	-0.01 (23)
Summer	-0.045 (27)	-0.406 (35)	0.329 (27)
Autumn	0.038 (30)	0.23 (24)	0.147 (23)
Winter	-0.537 (30)	-0.186 (32)	-0.034 (27)
Value of n is shown in parenthesis			

4.5.3 Atmospheric pressure

Significant relationships exist between atmospheric pressure and indoor ($R^2 = 0.26$, $n = 130$, $p < 0.01$, f ratio = 8.19) and outdoor ($R^2 = 0.5$, $n = 119$, $p < 0.001$, f ratio = 38.72)

respirable particulate concentrations for Building One (Figures 4.22 and 4.23). However, no significant relationship has been observed between atmospheric pressure and indoor:outdoor ratio (Figure 4.24). When the results are broken down into seasons (Table 4.3), significant correlations are observed for outdoor concentrations during spring ($R^2 = 0.53$, $n = 24$, $p < 0.001$), summer ($R^2 = 0.39$, $n = 27$, $p < 0.001$) and winter ($R^2 = 0.67$, $n = 34$, $p < 0.001$). Indoor correlations are significant for summer ($R^2 = 0.54$, $n = 32$, $p < 0.001$) and autumn ($R^2 = 0.32$, $n = 35$, $p < 0.01$). Correlation coefficients calculated for indoor:outdoor ratio are highly variable and alter from being significant positive correlations during summer ($R^2 = 0.33$, $n = 23$, $p < 0.01$) and autumn ($R^2 = 0.25$, $n = 29$, $p < 0.02$) to significant negative correlations during winter ($R^2 = -0.47$, $n = 33$, $p < 0.001$).

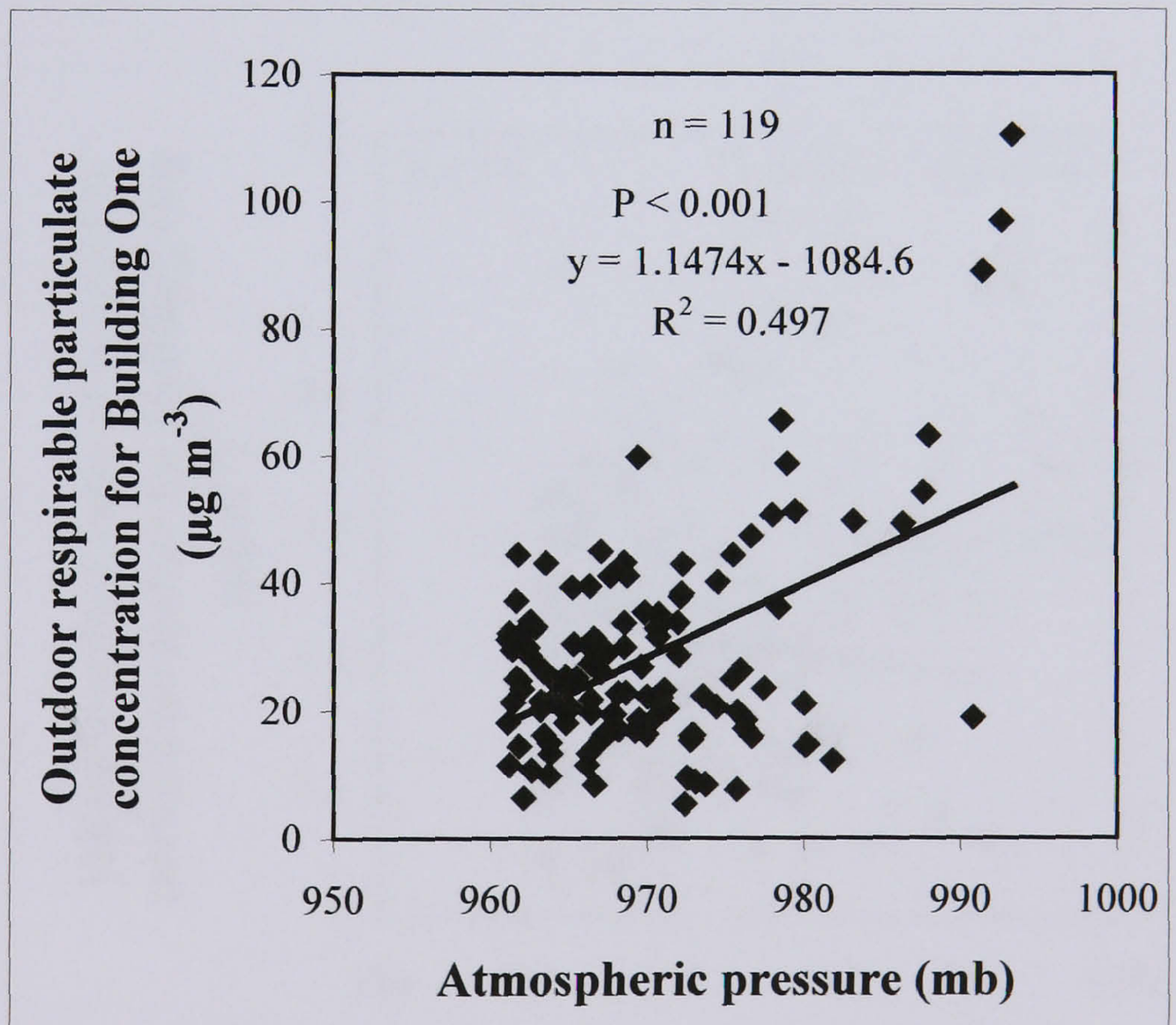


Figure 4.22: Regression analysis between outdoor concentrations of respirable particulate concentrations for Building One and atmospheric pressure

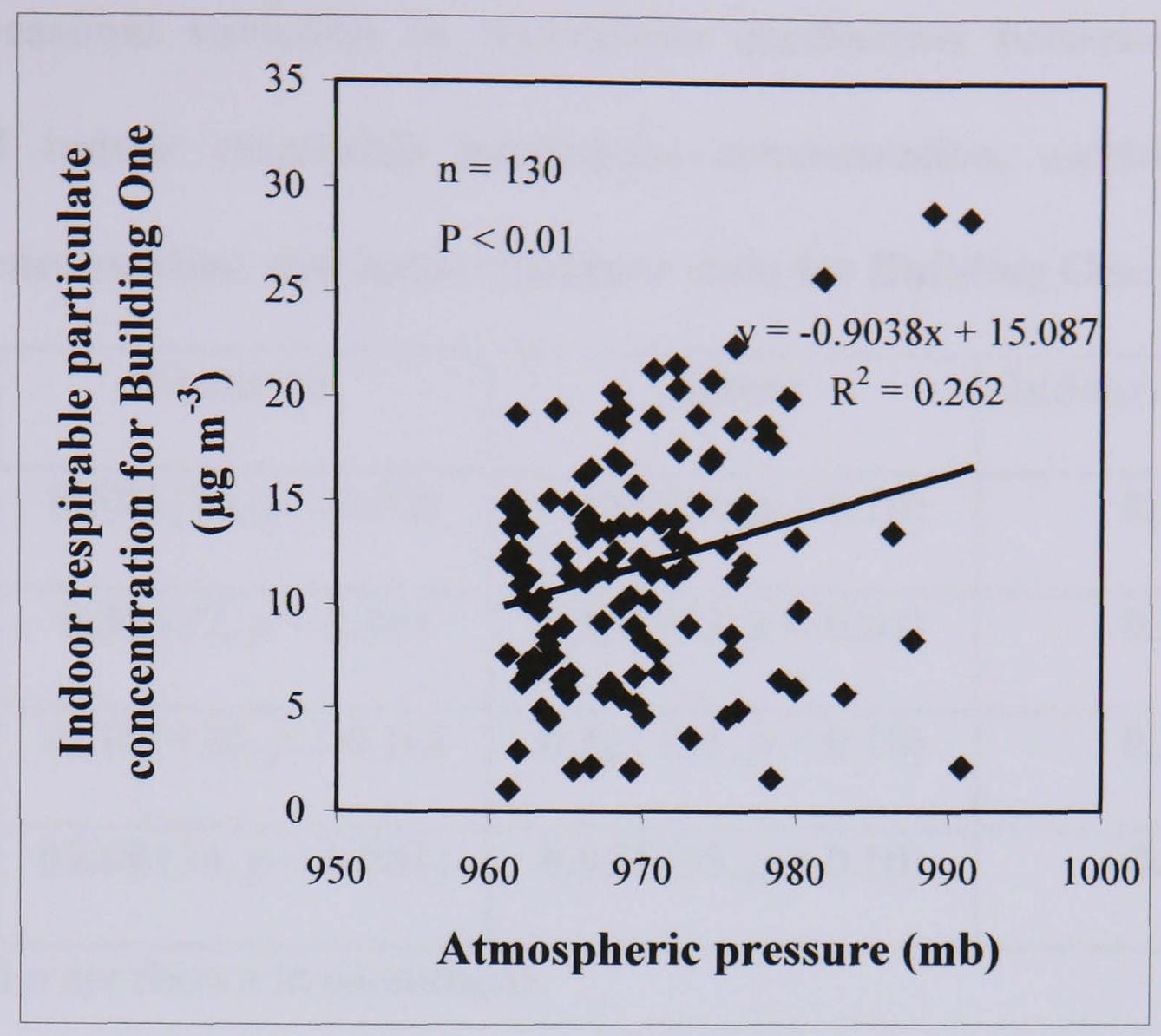


Figure 4.23: Regression analysis between indoor concentrations of respirable particulate concentrations for Building One and atmospheric pressure

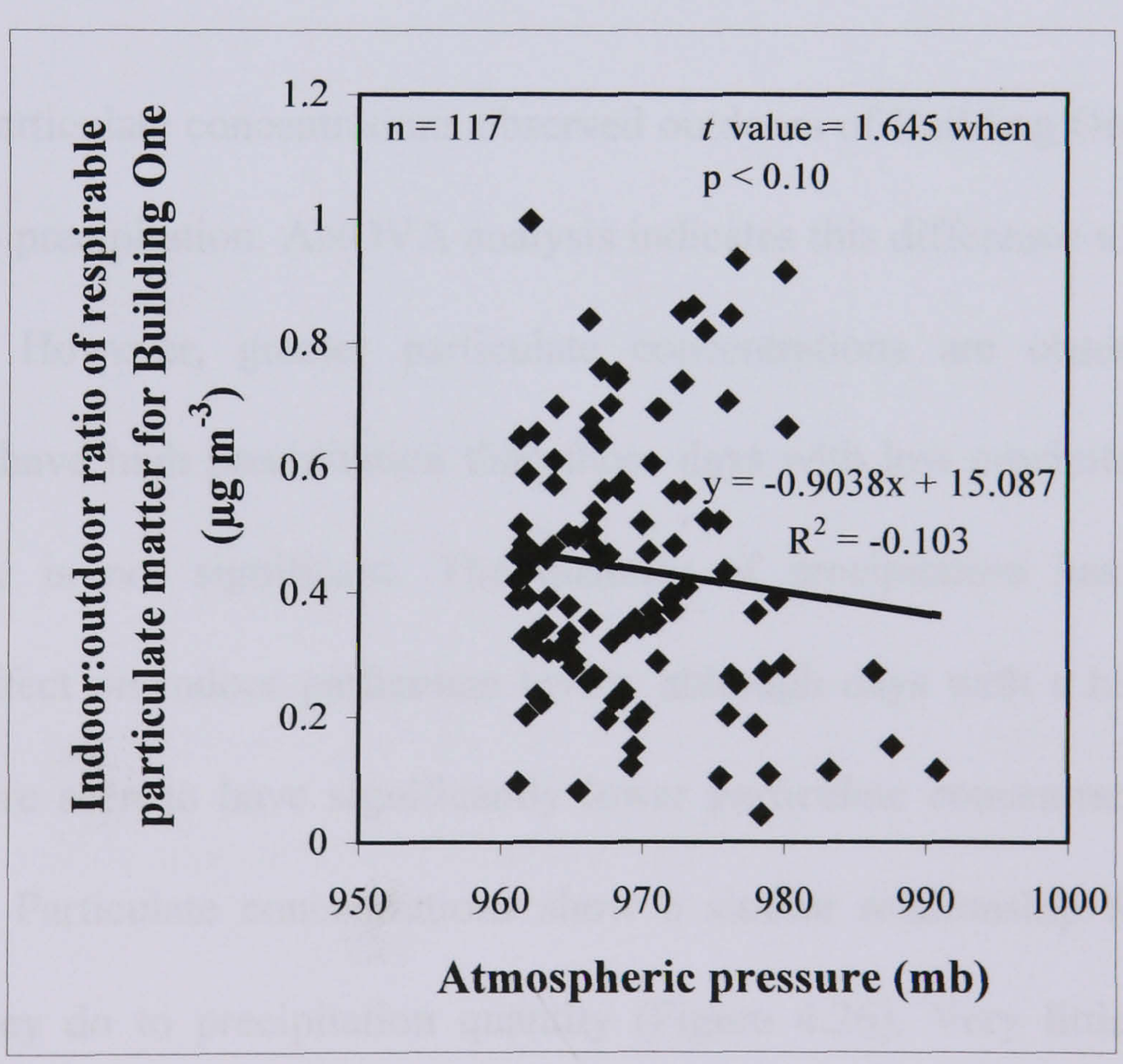


Figure 4.24: Regression analysis between indoor:outdoor ratio of respirable particulate matter for Building One and atmospheric pressure

Table 4.3: Seasonal variation in correlation coefficients between atmospheric pressure and indoor respirable particulate concentration, outdoor respirable particulate concentration and indoor:outdoor ratio for Building One

	Outdoor	Indoor	Indoor:outdoor ratio
Spring	**0.530** (24, $p < 0.02$)	**0.184** (24, $p < 0.10$)	**0.162** (22)
Summer	**0.39** (27, $p < 0.10$)	**0.536** (32, $p < 0.01$)	**0.326** (23)
Autumn	**-0.101** (30, $p > 0.10$)	**0.321** (35, $p < 0.10$)	**0.254** (29)
Winter	**0.668** (34, $p < 0.001$)	**0.047** (35, $p > 0.10$)	**-0.473** (33)
Value of n and p are shown in parenthesis.			

4.5.4 Precipitation and percentage relative humidity

The greatest particulate concentrations observed outdoors of Building One occur during days with zero precipitation. ANOVA analysis indicates this difference to be significant ($p < 0.001$). However, greater particulate concentrations are observed for days considered to have high precipitation than those days with low precipitation, although this difference is not significant. The quantity of precipitation has a much less pronounced affect on indoor particulate levels, although days with a high quantity of precipitation are seen to have significantly lower particulate concentrations ($p < 0.1$) (Figure 4.25). Particulate concentrations show a similar relationship to precipitation duration as they do to precipitation quantity (Figure 4.26). Very little difference in indoor concentrations is associated with precipitation duration, whereas, outdoors the

greatest particulate concentrations are observed during zero precipitation with a slight increase occurring during days with a long precipitation event.

Rainfall intensity (calculated as mm of rain falling per hour) appears to have no apparent affect upon indoor ($R^2 < 0.05$) or outdoor ($R^2 < 0.1$) particulate concentrations. In addition, particulate concentrations show no discernable relationship to relative humidity either indoors ($R^2 < 0.05$) or outdoors ($R^2 < 0.1$) of Building One.

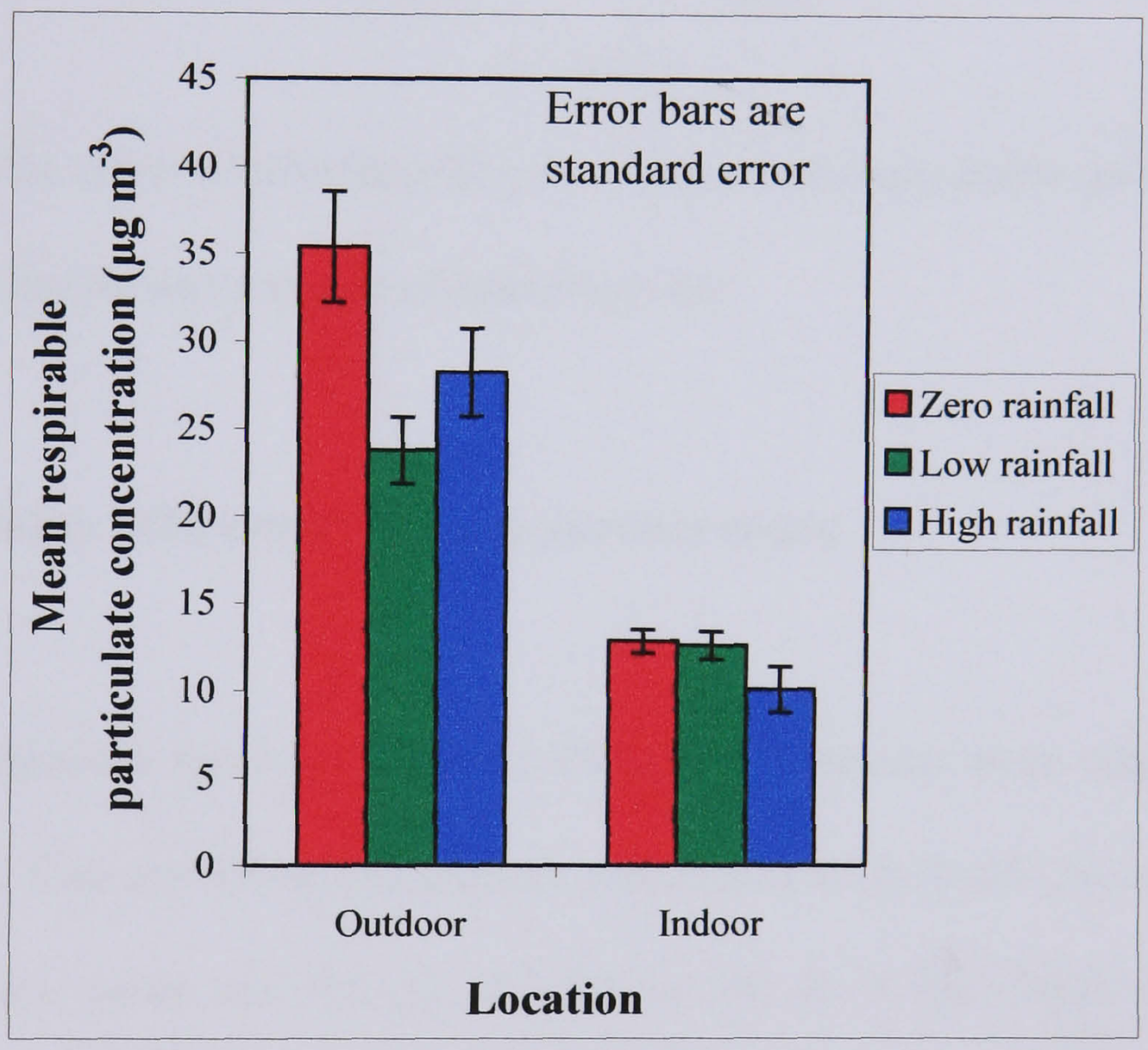


Figure 4.25: The effect of precipitation quantity on the respirable particulate concentration inside and outside of Building One

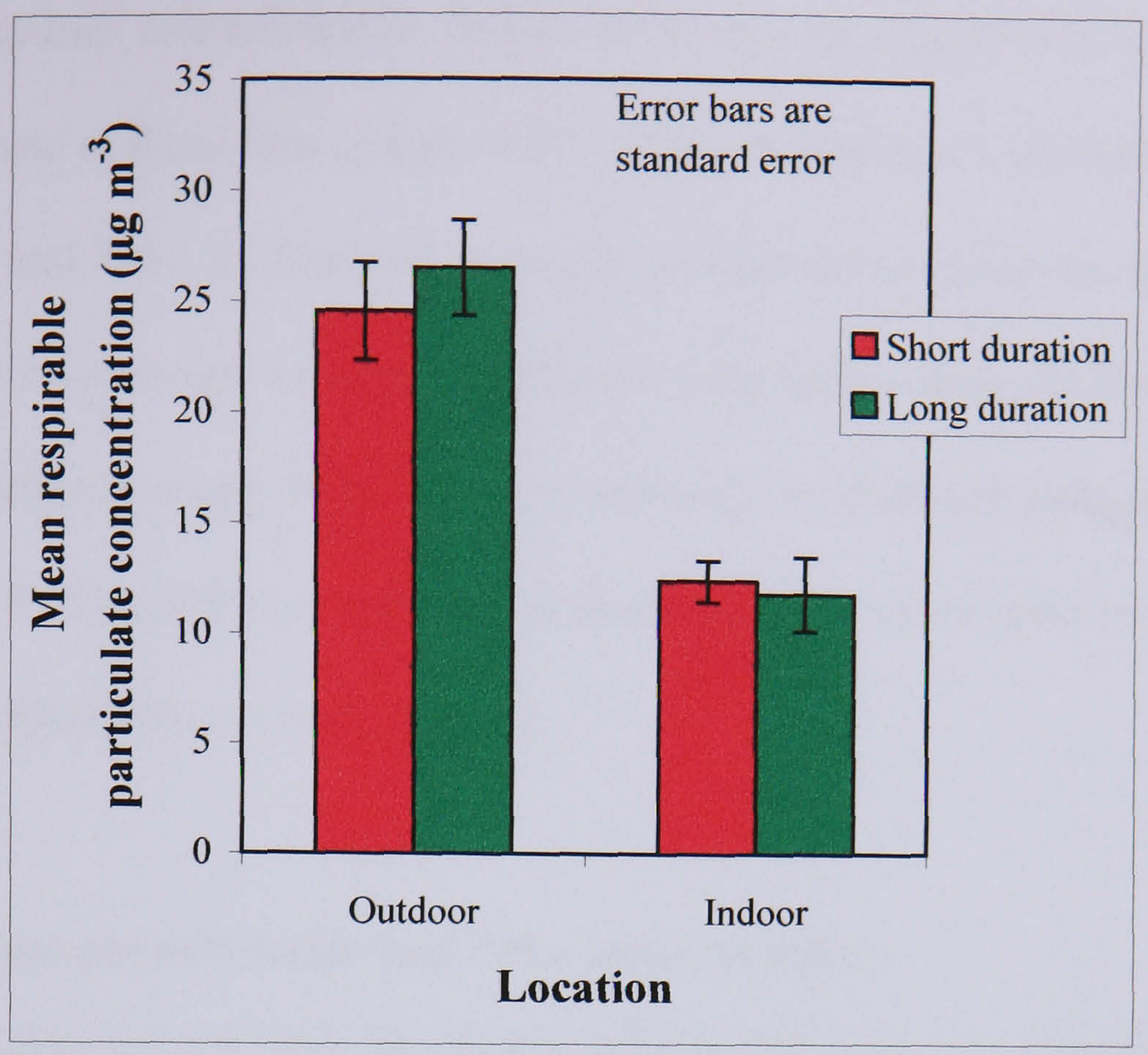


Figure 4.26: The effect of precipitation duration on the respirable particulate concentration inside and outside of Building One

4.6 Relationships between PM_{10} and particle count

24 hour, simultaneous particle count and PM_{10} measurements were taken from inside Buildings One, Two and Three and outdoor measurements at Road One and Road Two. The mean particle count and PM_{10} concentrations for all of the locations are shown in Table 4.4. Particle count concentrations are significantly greater inside Building Two than in either Building One or Building Three, with the concentrations inside Building Three significantly lower ($n = 42$, $p < 0.001$), this is also mirrored in PM_{10} concentrations. Both particle count and PM_{10} is significantly greater at Road One ($n = 42$, $p < 0.001$). At all locations a significant relationship is observed between PM_{10} and particle count. At all locations night time levels of both PM_{10} and particle count are

lower than daytime concentrations. Inside Building One (Figure 4.27), Building Two (Figure 4.28) and at Road One (Figure 4.30) a clear morning and afternoon peak in both particle count and PM_{10} is observed, however, particle count increases slightly ahead of PM_{10} and also takes longer to decrease following the peak values. At Road One (Figure 4.29), unlike particle count, PM_{10} shows no morning or afternoon peak. Inside Building Three (Figure 4.31) a different variation is observed; with no morning or afternoon peak occurring for either PM_{10} or particle count.

Table 4.4: Mean particle count and PM_{10} concentrations

Location	Particle count (cm^2)	PM_{10}
Building One	24634 (141)	17.7 (0.14)
Building Two	34560 (182)	21.6 (0.19)
Building Three	12792 (74)	12.9 (0.09)
Road One	37406 (190)	30.7 (0.24)
Road Two	14000 (62)	15.5 (0.10)
SE is shown in parenthesis		

Table 4.5: Correlation coefficients between PM_{10} and particle count

Location	Correlation Coefficient
Building One	0.50 ($p < 0.001$)
Building Two	0.56 ($p < 0.001$)
Building Three	0.76 ($p < 0.001$)
Road One	0.56 ($p < 0.001$)
Road Two	0.69 ($p < 0.001$)
$n = 48$	

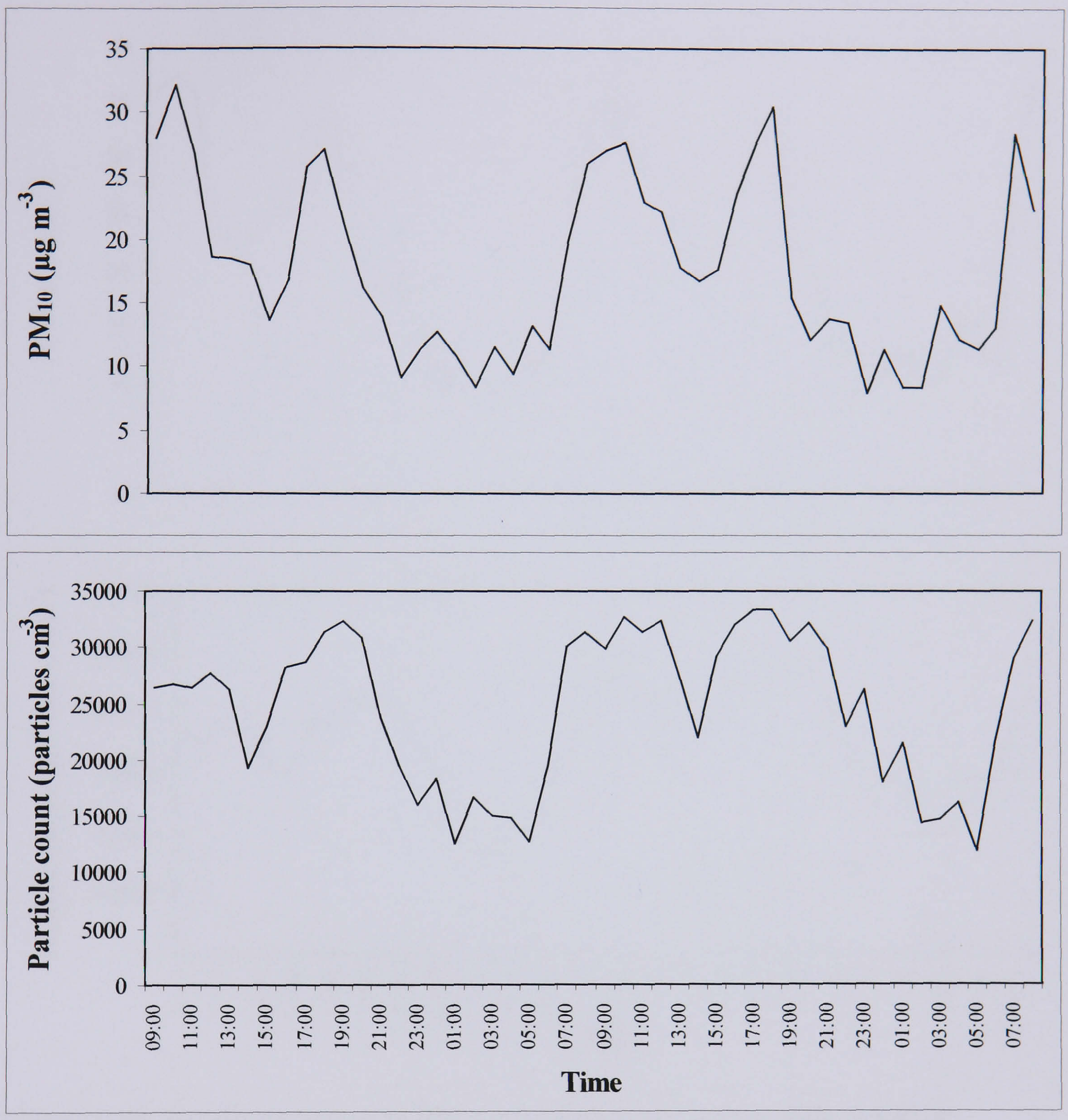


Figure 4.27: Hourly variation in PM_{10} concentrations and particle count for Building One

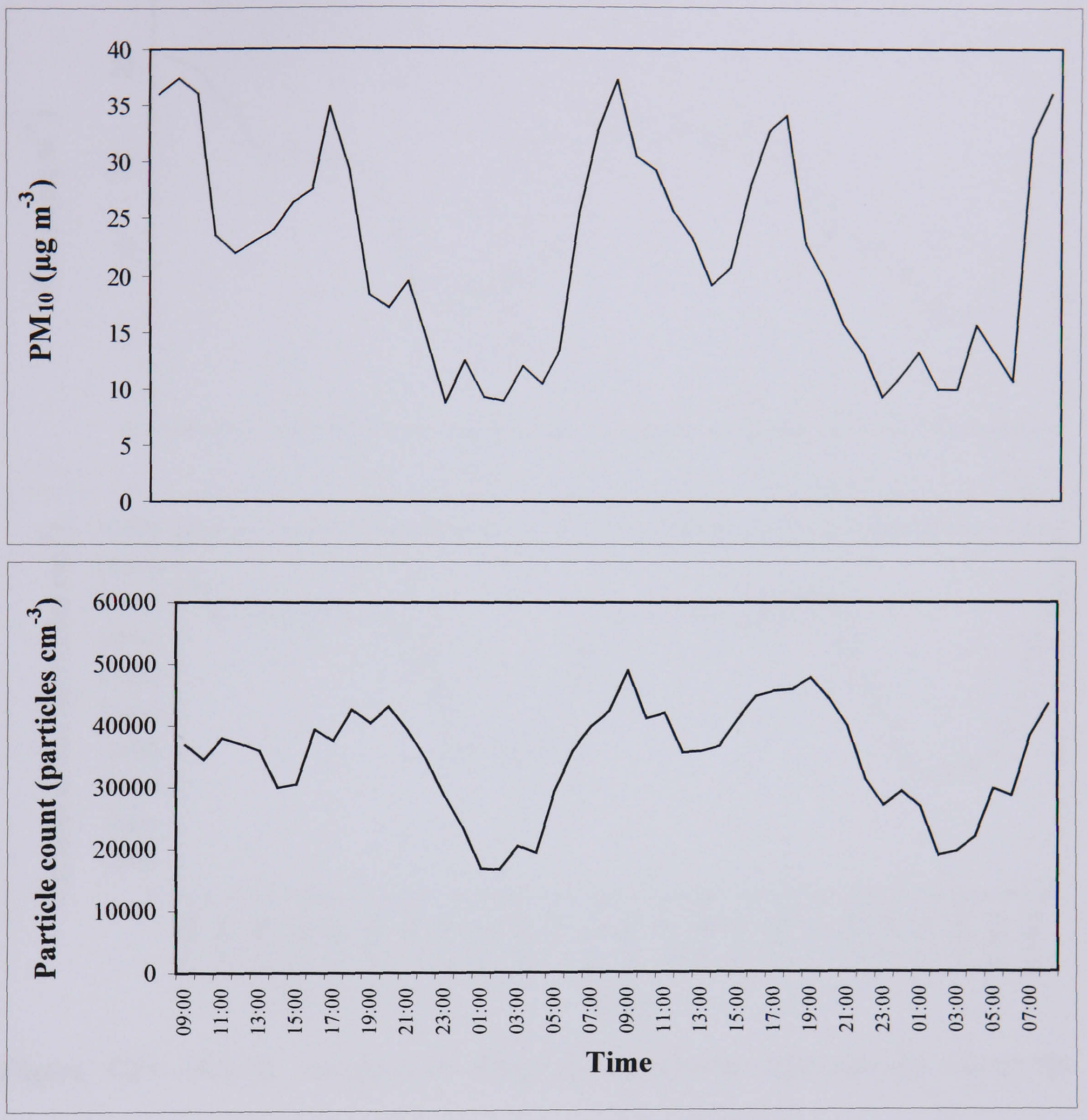


Figure 4.28: Hourly variation in PM_{10} concentrations and particle count for Building Two

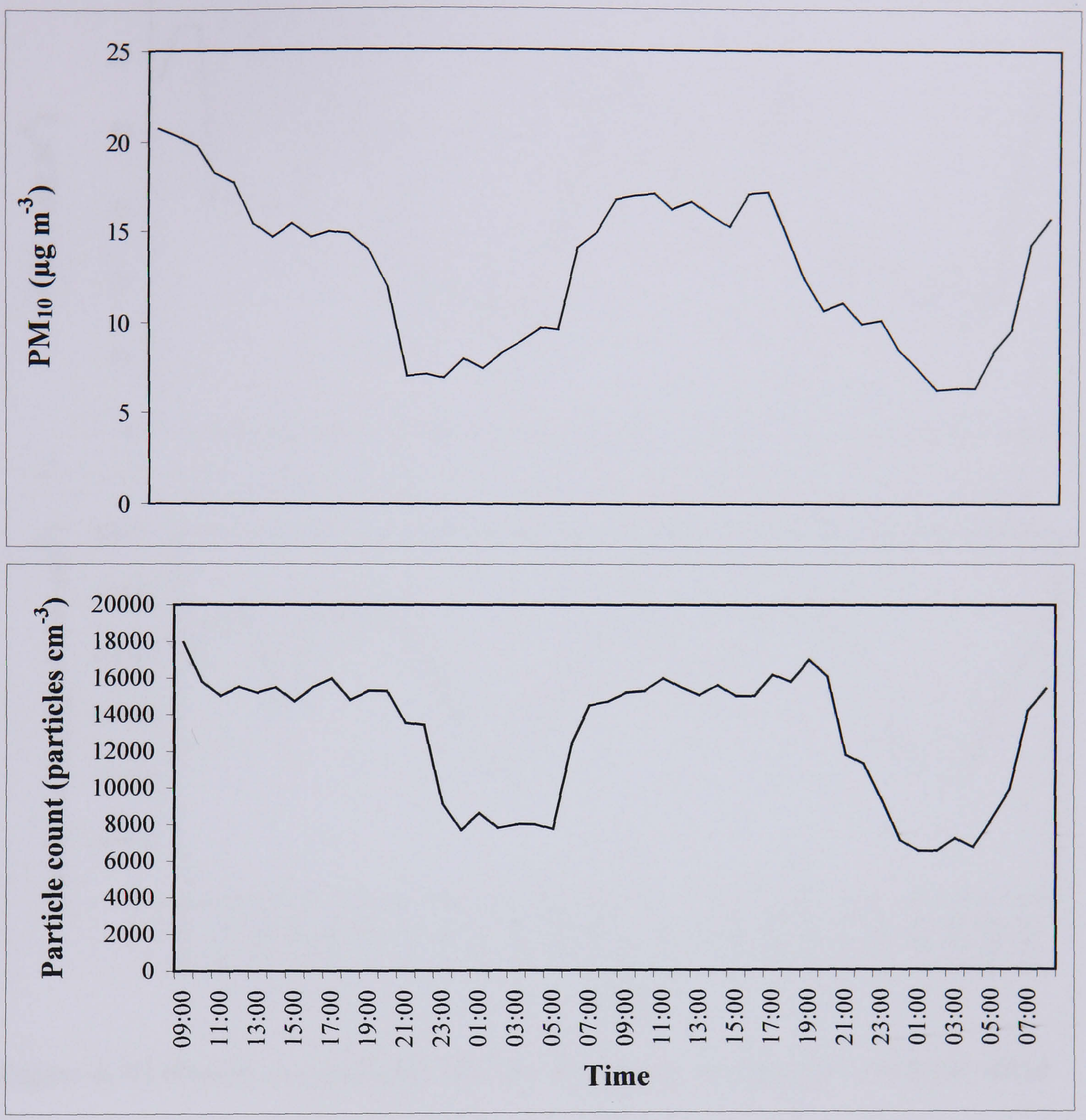


Figure 4.29: Hourly variation in PM_{10} concentrations and particle count for Building Three

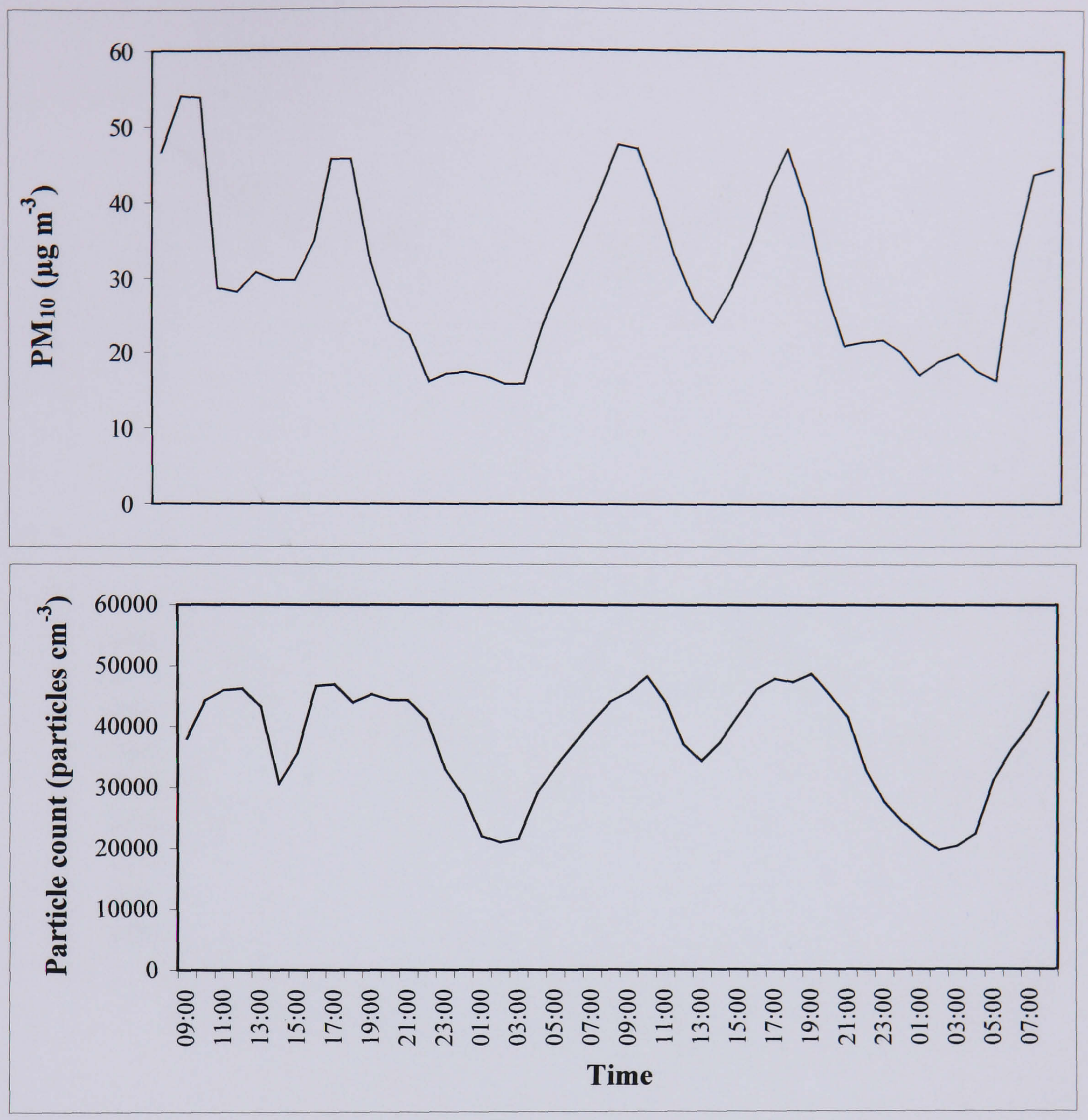


Figure 4.30: Hourly variation in PM_{10} concentrations and particle count for Road One

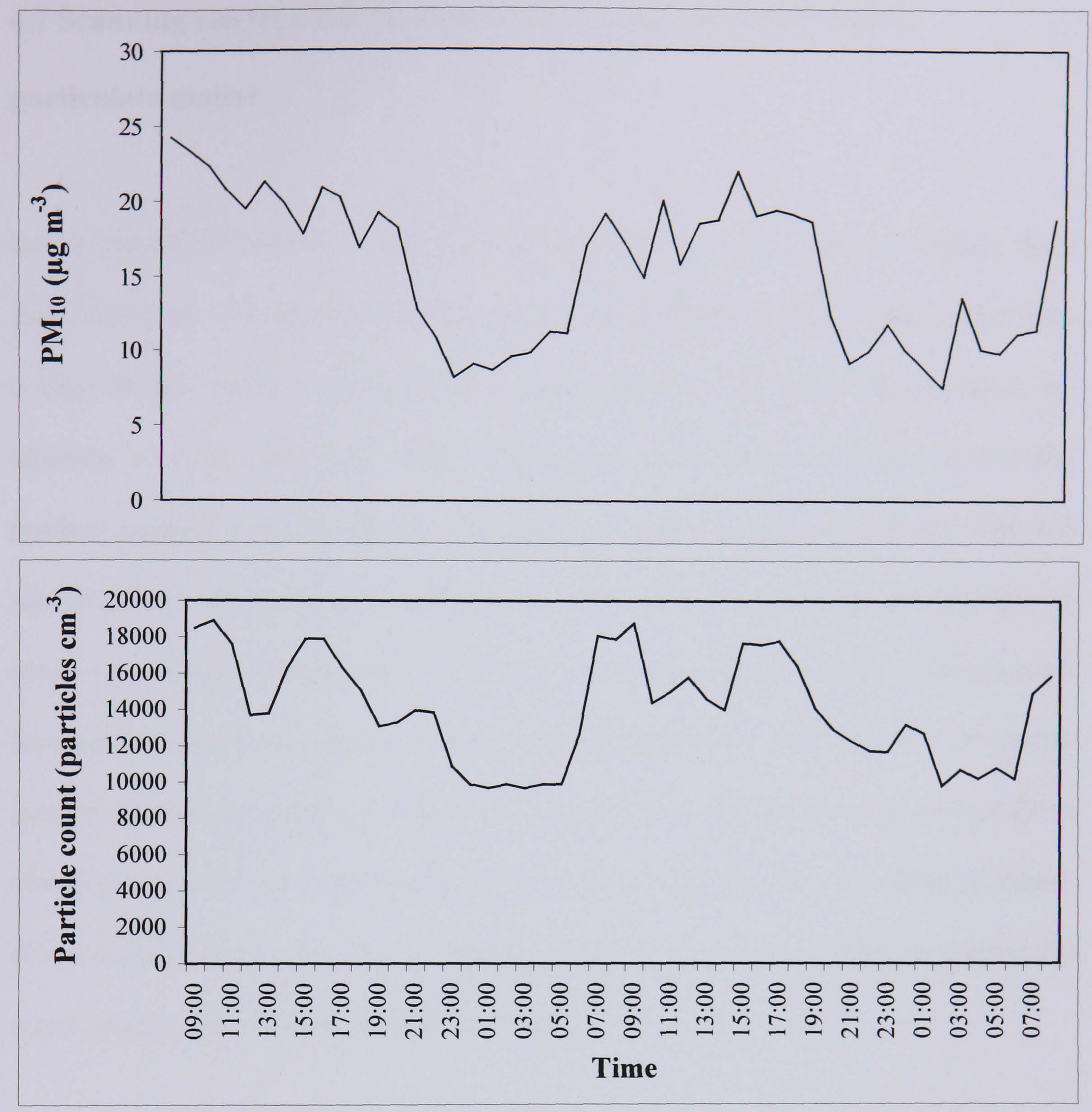


Figure 4.31: Hourly variation in PM_{10} concentrations and particle count for Road Two

4.7 Scanning electron microscopy of indoor and outdoor airborne particulate matter

Indoor respirable particulate samples from Building One and outdoor samples from Road One were simultaneously collected on nucleopore filter papers. These filters have a very smooth surface, allowing visual examination of the collected particulate by scanning electron microscope. Many micrographs were taken of several indoor and outdoor samples and the same type of particles (sub-micron spherical particles and accumulations of very fine particles) were observed to be present on the majority of occasions. Outdoor samples were dominated by accumulations of very small particles forming larger particles of up to 5 or 6 μm in diameter (Plate 4.1). Very few crystalline particles were observed for the Road One samples. Similarly, indoor samples from Road One also contained the same type of accumulations, with very few crystalline structures (Plate 4.2). However, the size of particle formed by the accumulations was generally much smaller indoors, often being sub-micron.

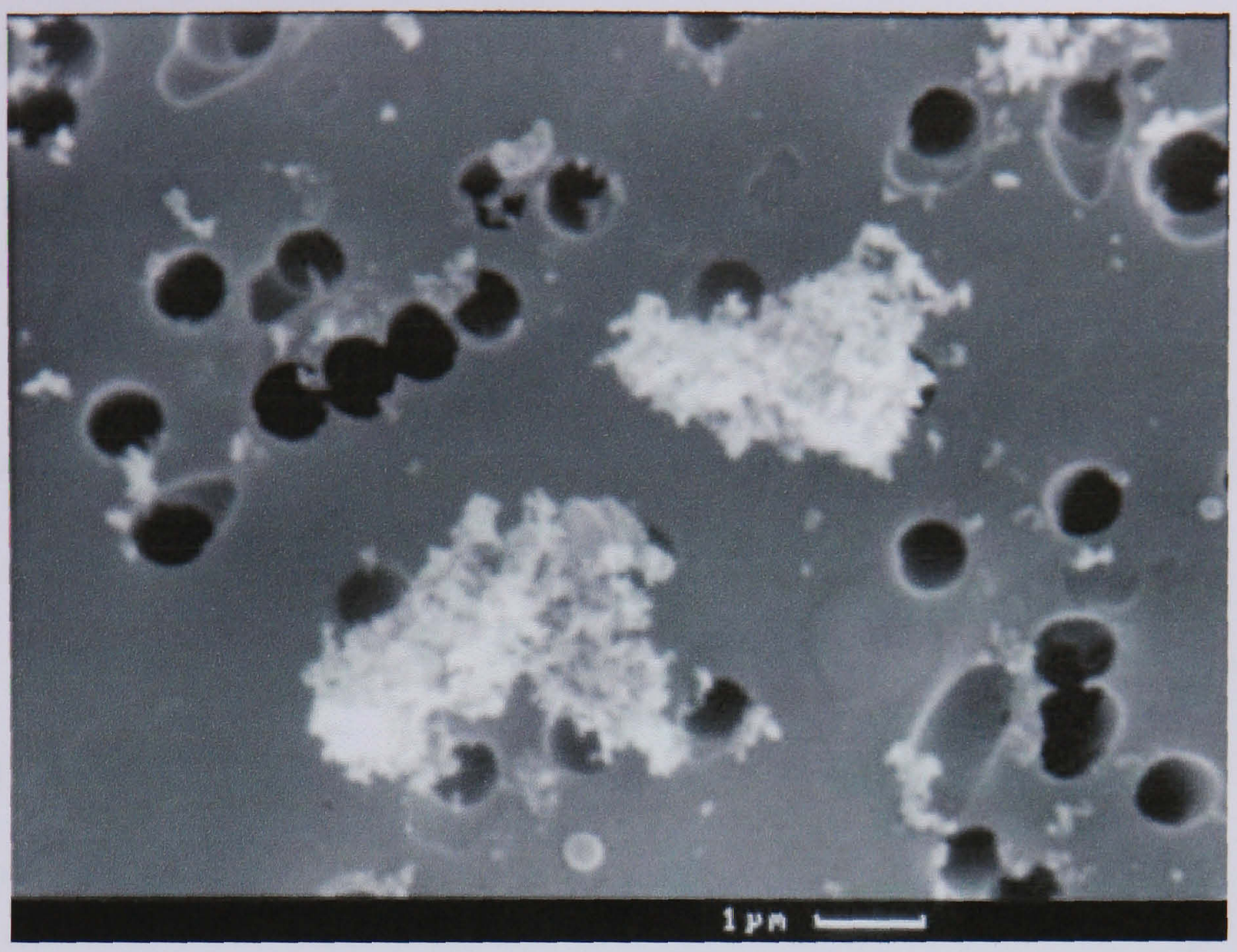


Plate 4.1: Scanning electron micrograph of outdoor airborne particulate (Magnification = 10,000)

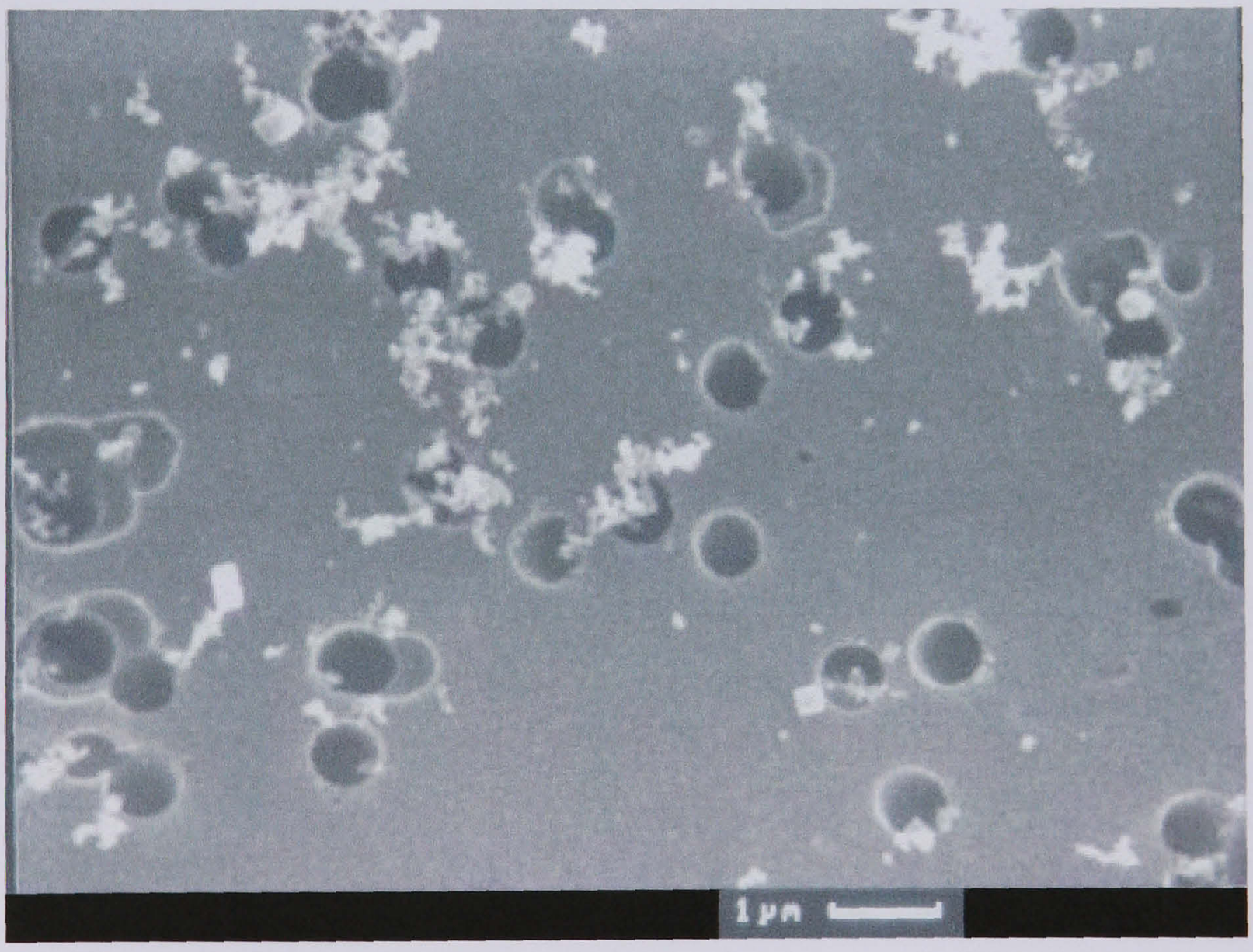


Plate 4.2: Scanning electron micrograph of indoor airborne particulate (Magnification = 10,000)

4.8 Chemical analysis of indoor and outdoor airborne particulate matter

4.8.1 Elemental analysis

Elemental analysis of respirable particulate matter collected inside and outside of Building One shows some noticeable relationships between the analysed elements (Tables 4.6 to 4.6). For indoor particulates the only significant correlation exists between Zn and Cu ($n = 82$, $p < 0.001$), none of the other elements analysed display any significant relationship (Table 4.8). In particulates collected outdoors, several elements display significant correlations (Table 4.7), with the most significant being between Al and Ca, Al and Mn and also between Cu and Zn ($n = 83$, $p < 0.001$).

Several elements, including Cu, Fe, Pb and Zn ($n = 83$, $p < 0.001$), also show significant correlations between indoors and outdoors (Table 4.8). Interestingly, indoor Cu concentrations are also significantly correlated to outdoor Zn concentrations ($n = 82$, $p < 0.001$). Other elements also show this relationship, but the correlations are not so strong. There is a noticeable difference in the indoor:outdoor ratio between the elements, with Cu (0.56), Mg (0.46), Pb (0.55) and Zn (0.57) showing greater indoor:outdoor ratios than the other elements.

There appears to be no discernable seasonal variation in elemental concentrations, indoors or outdoors (Table 4.10 and 4.11), with seasonal variations in elemental concentrations being relatively small.

Table 4.6: Correlation matrix of respirable particulate chemistry inside Building One

	Al	Ca	Cu	Fe	K	Mg	Mn	Pb	Zn
Al	*	0.01	0.08	0.16	0.03	0.16	0.15	0.10	0.18
Ca		*	0.14	0.06	0.17	0.03	0.06	0.01	0.15
Cu			*	0.17	0.18	0.11	0.03	0.19	0.32
Fe				*	<0.1	<0.1	0.18	0.10	0.12
K					*	0.21	0.05	0.02	0.02
Mg						*	0.18	0.16	0.15
Mn							*	0.17	0.07
Pb								*	0.01
Zn									*
$n = 72, p < 0.05 = 0.232, p < 0.01 = 0.302, p < 0.001 = 0.380$									

Table 4.7: Correlation matrix of respirable particulate chemistry outside Building One

	Al	Ca	Cu	Fe	K	Mg	Mn	Pb	Zn
Al	*	0.78	0.42	0.07	0.15	0.27	0.54	0.02	0.63
Ca		*	0.44	0.01	0.01	0.34	0.62	0.05	0.40
Cu			*	0.08	0.12	0.05	0.23	0.06	0.69
Fe				*	0.16	0.13	0.01	0.28	0.10
K					*	0.12	0.16	0.14	0.10
Mg						*	0.17	0.04	0.06
Mn							*	0.20	0.26
Pb								*	0.01
Zn									*
$n = 72, p < 0.05 = 0.232, p < 0.01 = 0.302, p < 0.001 = 0.380$									

Table 4.8: Correlation matrix of indoor and outdoor respirable particulate elemental concentrations for Building One

	Outdoor								
Indoor	**Al**	**Ca**	**Cu**	**Fe**	**K**	**Mg**	**Mn**	**Pb**	**Zn**
Al	0.26	0.38	0.36	0.05	0.02	0.02	0.12	0.13	0.17
Ca		0.22	0.32	0.02	0.01	0.09	0.14	0.02	0.17
Cu			0.61	0.08	0.01	0.04	0.18	0.06	0.41
Fe				0.44	0.07	0.17	0.01	0.26	0.19
K					0.25	0.23	0.08	0.01	0.12
Mg						0.14	0.03	<0.01	0.14
Mn							0.26	0.18	0.04
Pb								0.68	0.01
Zn									0.62
$n = 72$, $p < 0.05 = 0.232$, $p < 0.01 = 0.302$, $p < 0.001 = 0.380$									

Table 4.9: Mean indoor and outdoor respirable particulate elemental concentrations and indoor:outdoor ratio

	Indoor		Outdoor		Indoor:outdoor ratio
	Mean	**SE**	**Mean**	**SE**	
Al	26.0	2.04	161.5	16.27	0.16
Ca	20.6	1.58	105.7	8.89	0.20
Cu	26.9	2.15	46.0	4.66	0.56
Fe	52.9	1.48	164.7	2.26	0.32
K	17.0	0.96	77.4	1.76	0.22
Mg	69.2	2.66	150.1	3.32	0.46
Mn	16.0	1.28	56.0	3.12	0.29
Pb	88.0	2.24	158.9	2.92	0.55
Zn	35.0	3.29	61.3	5.54	0.57
($n = 72$) Concentrations in ng m^{-3}					

Table 4.10: Seasonal variation in respirable particulate elemental concentrations inside Building One

	Spring (n = 17)	Summer (n = 20)	Autumn (n = 16)	Winter (n = 19)
Al	30.7 (3.88)	29.9 (4.1)	16.9 (3.4)	30.6 (4.9)
Ca	23.8 (4.4)	21.9 (3.2)	18.8 (3.2)	18.8 (2.3)
Cu	22.5 (3.6)	25.6 (3.7)	21.0 (4.2)	33.9 (5.4)
Fe	49.2 (3.5)	55.4 (3.6)	55.0 (2.4)	49.8 (2.7)
K	14.4 (2.4)	18.1 (1.9)	17.2 (1.9)	18.1 (1.8)
Mg	67.9 (7.8)	67.7 (5.6)	68.0 (3.5)	72.6 (6.3)
Mn	18.0 (2.8)	17.8 (2.6)	14.6 (2.5)	14.9 (2.7)
Pb	83.8 (5.6)	91.2 (5.5)	85.2 (3.6)	92.4 (4.1)
Zn	30.3 (5.2)	48.2 (10.3)	28.0 (5.1)	34.1 (4.5)
Concentrations in ng m^{-3} (Standard error shown in parenthesis)				

Table 4.11: Seasonal variation in respirable particulate elemental concentrations outside Building One

	Spring (n = 17)	Summer (n = 20)	Autumn (n = 16)	Winter (n = 19)
Al	181.0 (40.8)	200.9 (46.8)	102.0 (15.7)	175.2 (28.2)
Ca	131.5 (28.77)	112.4 (14.4)	70.1 (8.04)	118.7 (21.46)
Cu	44.7 (11.19)	53.0 (10.52)	36.9 (7.95)	52.2 (9.90)
Fe	163.6 (5.58)	165.7 (4.33)	167.6 (4.07)	159.5 (4.97)
K	75.2 (3.72)	78.7 (3.84)	77.7 (3.49)	77.8 (3.77)
Mg	146.5 (8.76)	151.8 (6.57)	151.3 (6.03)	152.8 (6.62)
Mn	53.3 (6.44)	60.2 (5.76)	50.7 (5.64)	58.9 (7.97)
Pb	159.2 (8.61)	158.3 (7.04)	157.3 (4.07)	162.2 (4.66)
Zn	53.6 (8.39)	86.8 (17.42)	47.2 (8.04)	61.0 (7.74)
Concentrations in ng m^{-3} (Standard error shown in parenthesis)				

4.8.2 Anion analysis

Correlation coefficients determined between indoor and outdoor anion concentrations show that there is a clear difference between the analytes. Sulphate displays a clear relationship with a correlation coefficient of 0.65 ($p < 0.001$), with nitrate also displaying a significant correlation ($r = 0.44$, $p < 0.001$), whereas, chloride does not show any significant relationship ($r = 0.23$, $p < 0.10$). These results are also mirrored in the indoor:outdoor ratios calculated for each anion (Table 4.12), with sulphate (0.64) and nitrate (0.51) both having relatively high indoor:outdoor ratios when compared to chloride (0.21).

Seasonal variations in anion concentration are also observed with, generally, the same trends being seen for both indoor and outdoor respirable particulate matter (Table 4.13 and 4.14). Chloride concentrations are greatest during the winter months and then gradually decrease throughout spring, summer and autumn. Both nitrate and sulphate concentrations are greatest during the summer months and at their lowest during the winter.

Table 4.12: Mean indoor and outdoor anion concentrations and indoor:outdoor ratio

	Indoor		Outdoor		Indoor:outdoor ratio
	Mean	**SE**	**Mean**	**SE**	
Chloride	145	38.77	680	35.95	0.21
Nitrate	744	59.92	1459	113.59	0.51
Sulphate	2756	176.99	4324	258.38	0.64
($n = 72$) Concentrations in ng m^{-3}					

Table 4.13: Seasonal variations in outdoor anion concentrations

	Spring (*n* = 17)	Summer (*n* = 20)	Autumn (*n* = 16)	Winter (*n* = 19)
Chloride	723 (82)	651 (40)	647 (79)	735 (57)
Nitrate	1489 (277)	1726 (229)	1344 (204)	1250 (192)
Sulphate	4099 (645)	5212 (404)	3880 (507)	4298 (466)
Concentrations in ng m^{-3} (Standard error shown in parenthesis)				

Table 4.14: Seasonal variations in indoor anion concentrations

	Spring (*n* = 17)	Summer (*n* = 20)	Autumn (*n* = 16)	Winter (*n* = 19)
Chloride	435 (437)	414 (288)	369 (361)	479 (327)
Nitrate	777 (144)	947 (132)	687 (116)	593 (89)
Sulphate	2611 (436)	3450 (288)	2457 (361)	2597 (327)
Concentrations in ng m^{-3} (Standard error shown in parenthesis)				

4.8.3 Chemical analysis of size fractionated airborne particulate matter

Airborne particulate matter of the size fractions TSP, PM_{10}, respirable particulates and $PM_{2.5}$ were collected inside the foyers of Buildings One, Two and Three. Samples were also collected outside at Road One and Road Two. These particulates were analysed for chloride, nitrate and sulphate and the percentage of total mass for each anion was determined.

From the analysis it is clear that sulphate comprises the majority of airborne particulate mass, typically being between 25 and 35%. Nitrate and chloride account for 5-10% and 4-6 % by particulate mass, respectively (Table 4.15).

Between the samples from the different locations the variation in composition is relatively small. However, there is a change in composition for particulates of different diameters with notable a rise in the percentage of sulphate in $PM_{2.5}$ observed at all locations except inside Building Three. Chloride and nitrate do not appear to display this relationship.

Table 4.15: Chemical composition of size fractionated airborne particulate matter expressed as a percentage of total mass

	TSP	PM_{10}	Respirable	$PM_{2.5}$
Road One (*n* = 31)				
Chloride	5.0	5.4	4.8	5.5
Nitrate	7.6	6.6	6.9	6.6
Sulphate	29.1	28.5	27.6	34.6
Road Two (*n* = 29)				
Chloride	4.9	4.8	5.4	4.6
Nitrate	7.0	6.0	6.3	6.2
Sulphate	26.4	26.7	27.0	33.9
Building One (*n* = 41)				
Chloride	4.7	5.0	4.9	5.5
Nitrate	7.1	7.4	7.6	7.6
Sulphate	27.8	26.5	27.7	31.4
Building Two (*n* = 30)				
Chloride	4.8	5.4	5.0	4.4
Nitrate	7.5	7.4	7.6	8.1
Sulphate	27.9	26.7	26.6	32.8
Building Three (*n* = 30)				
Chloride	4.8	5.2	5.0	5.3
Nitrate	7.4	8.5	8.5	9.2
Sulphate	28.0	28.4	28.1	28.7

4.9 Personal exposure

To assess personal exposure, respirable particulate measurements were taken for one individual working inside Building One for 20 working days between the hours of 0900 and 1700 hours with indoor and outdoor concentrations measured simultaneously. In addition, a height profile of particulate concentration was measured inside the main foyer of Building One (Figure 4.32). It is clear from the height profile measurements that the greatest airborne particulate concentrations exist in the breathing zone, with concentrations near to floor and ceiling height being significantly lower ($p < 0.001$).

Significant relationships exist between personal exposure and both indoor ($R^2 = 0.93$, $p < 0.001$, f ratio = 116.8) and outdoor ($R^2 = 0.69$, $p < 0.001$, f ratio = 16.47) particulate concentrations (Figure 4.33 and 4.34). However, the correlation is stronger between personal exposure and indoor measurements. Interestingly, the Y intercept for both correlations is approximately equal.

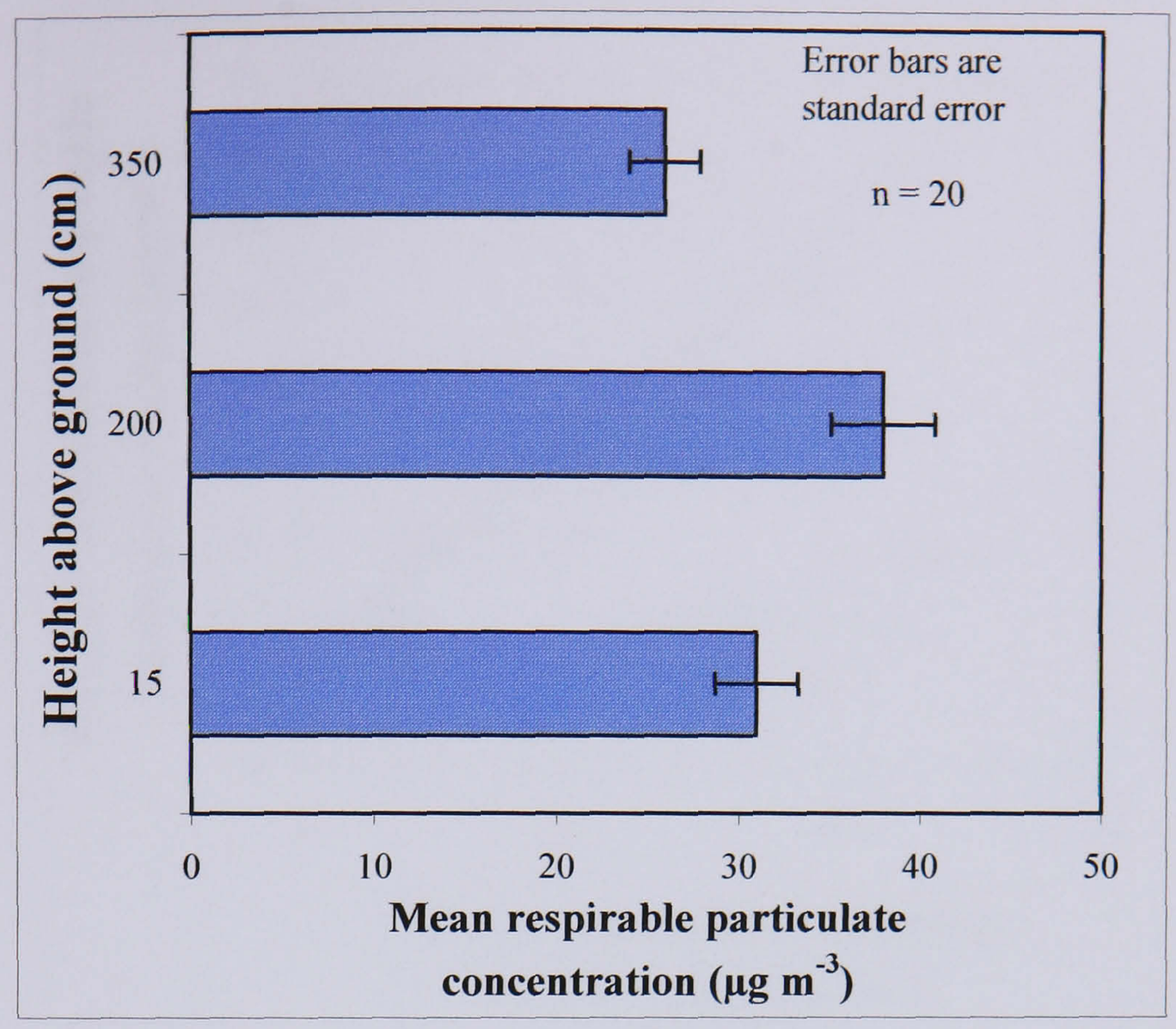


Figure 4.32 Height profile of respirable particulate concentrations in the foyer of Building One

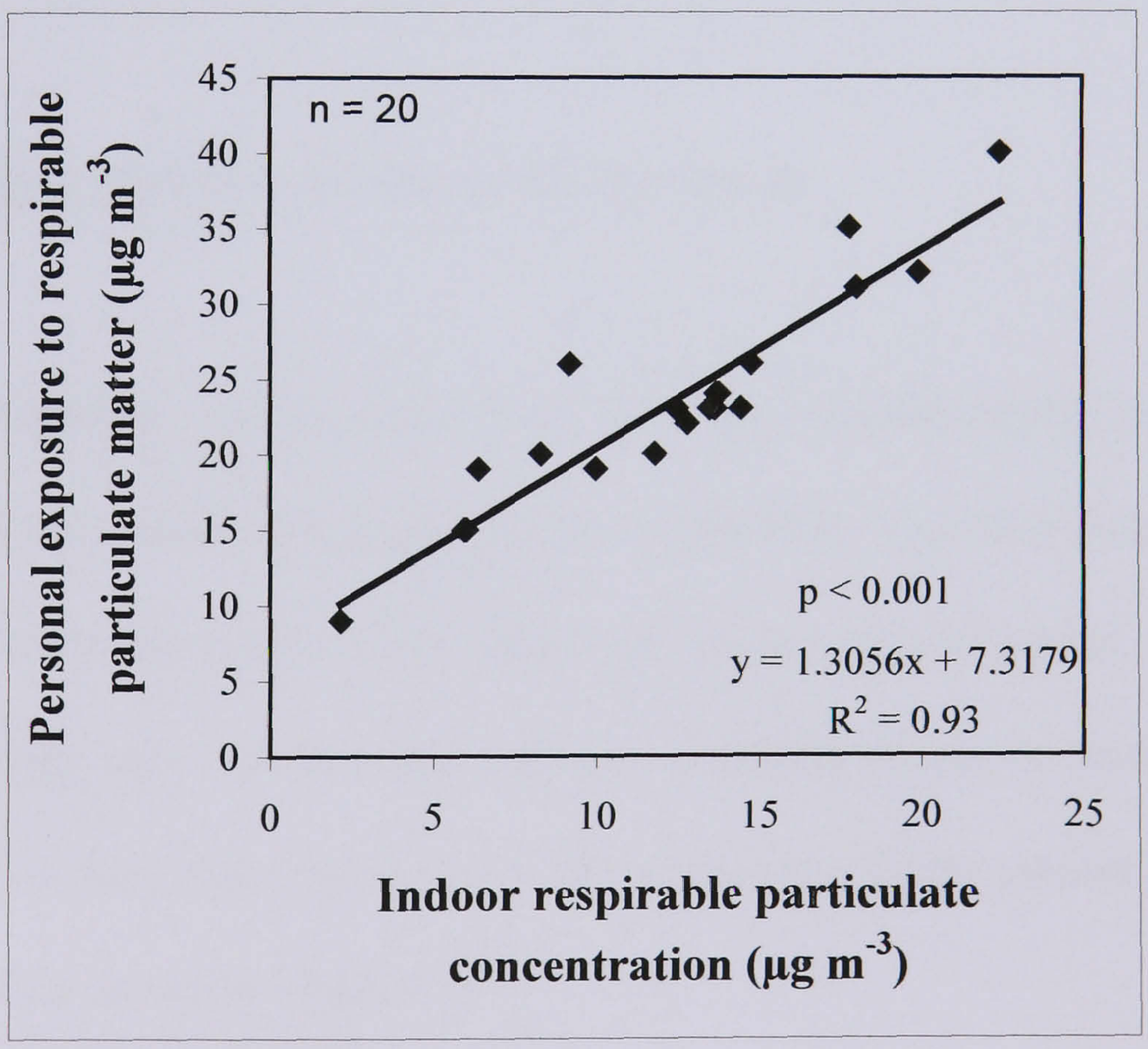


Figure 4.33: Regression analysis between indoor respirable particulate concentrations and personal exposure for Building One

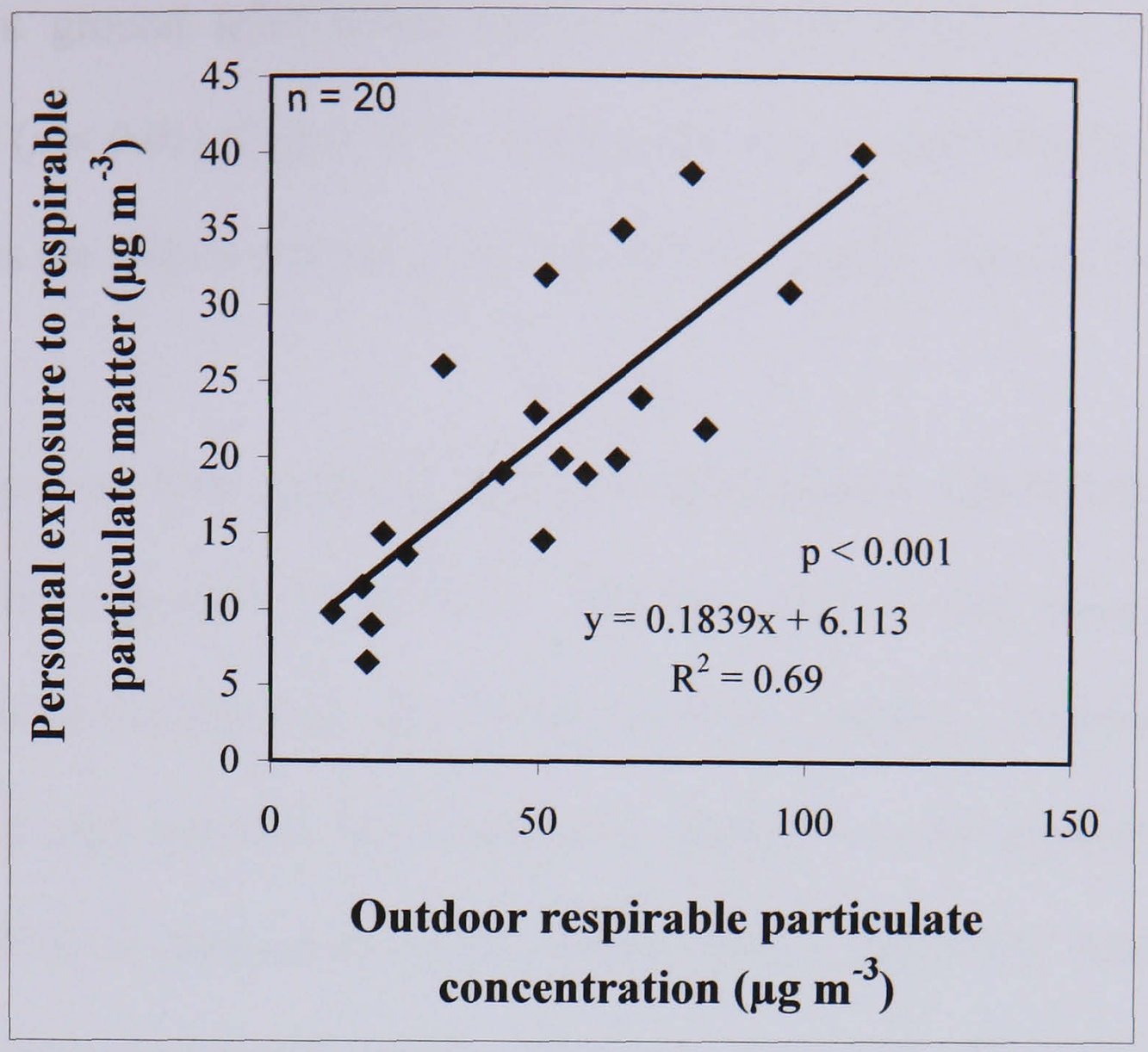


Figure 4.34: Regression analysis between outdoor respirable particulate concentrations and personal exposure for Building One

4.10 Particulate variation within a street canyon

Respirable particulate concentrations were measured simultaneously at four different locations within the Road One street canyon. In addition, wind direction was measured at the nearby meteorological station. Two particulate sampling points were at ground level on opposite sides of the road and two sampling points at roof level also on opposite sides of the road (Figure 4.35). The orientation of the canyon (approximately 110° E from N) is shown in Figure 4.36.

It is clear that ground level concentrations are significantly greater than roof top concentrations ($p < 0.01$) (Figure 4.37). Also, as expected, concentrations at each of the sampling points are well correlated to one another ($p < 0.001$) (Table 4.16).

Concentrations at all four sampling positions show distinct variations in response to changes in wind direction (Table 4.17). For the sake of data interpretation, wind direction has been classified as either being northerly, easterly, southerly or westerly. During easterly and westerly wind directions (parallel to the canyon), there is no significant pattern in particulate concentrations with a relatively small variation in concentration between sample points. However, for northerly and southerly wind directions (perpendicular to the canyon), north lower and south lower samples respectively are significantly greater ($p < 0.01$).

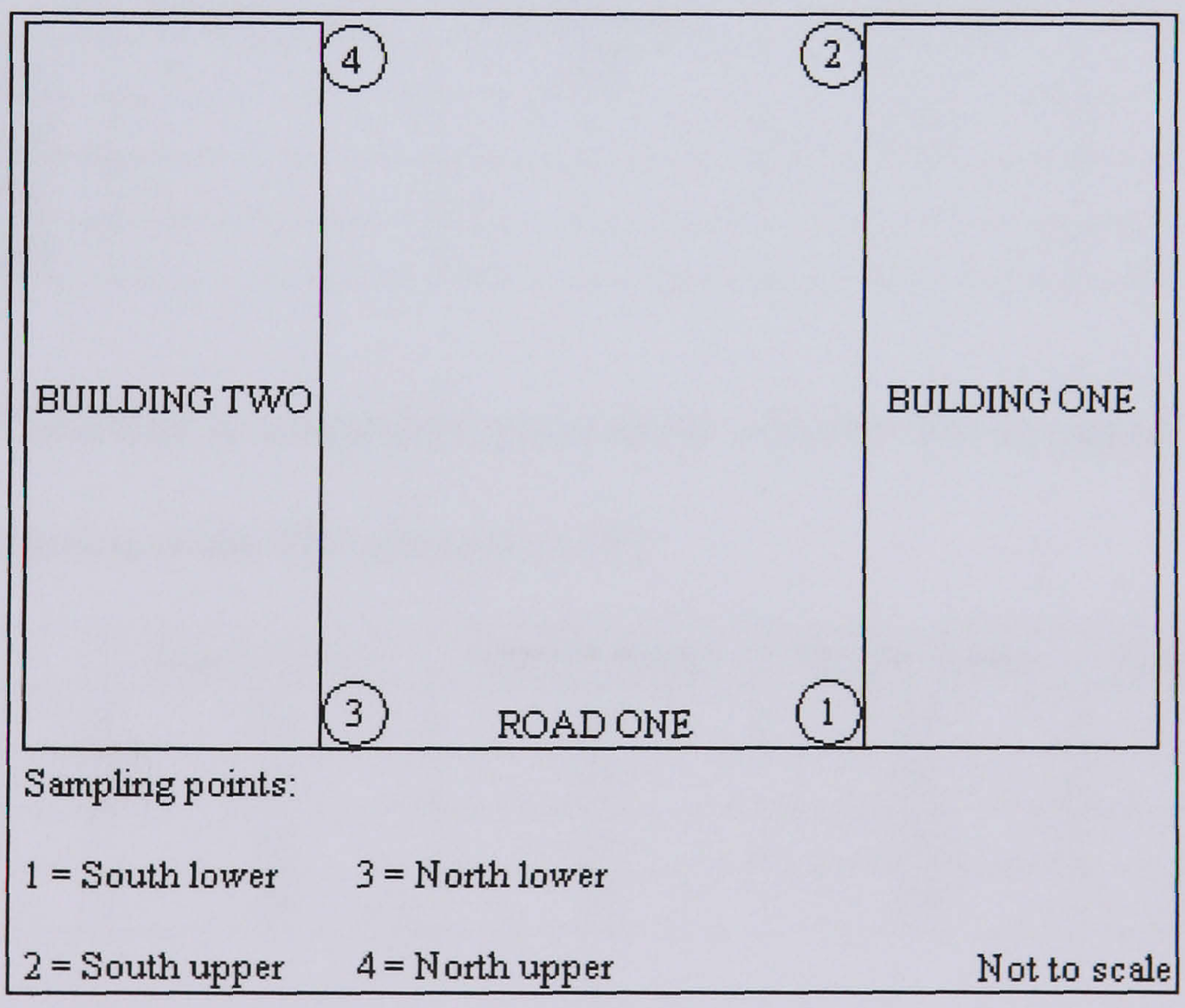


Figure 4.35: Cross section view of location of sampling points within the street canyon of Road One

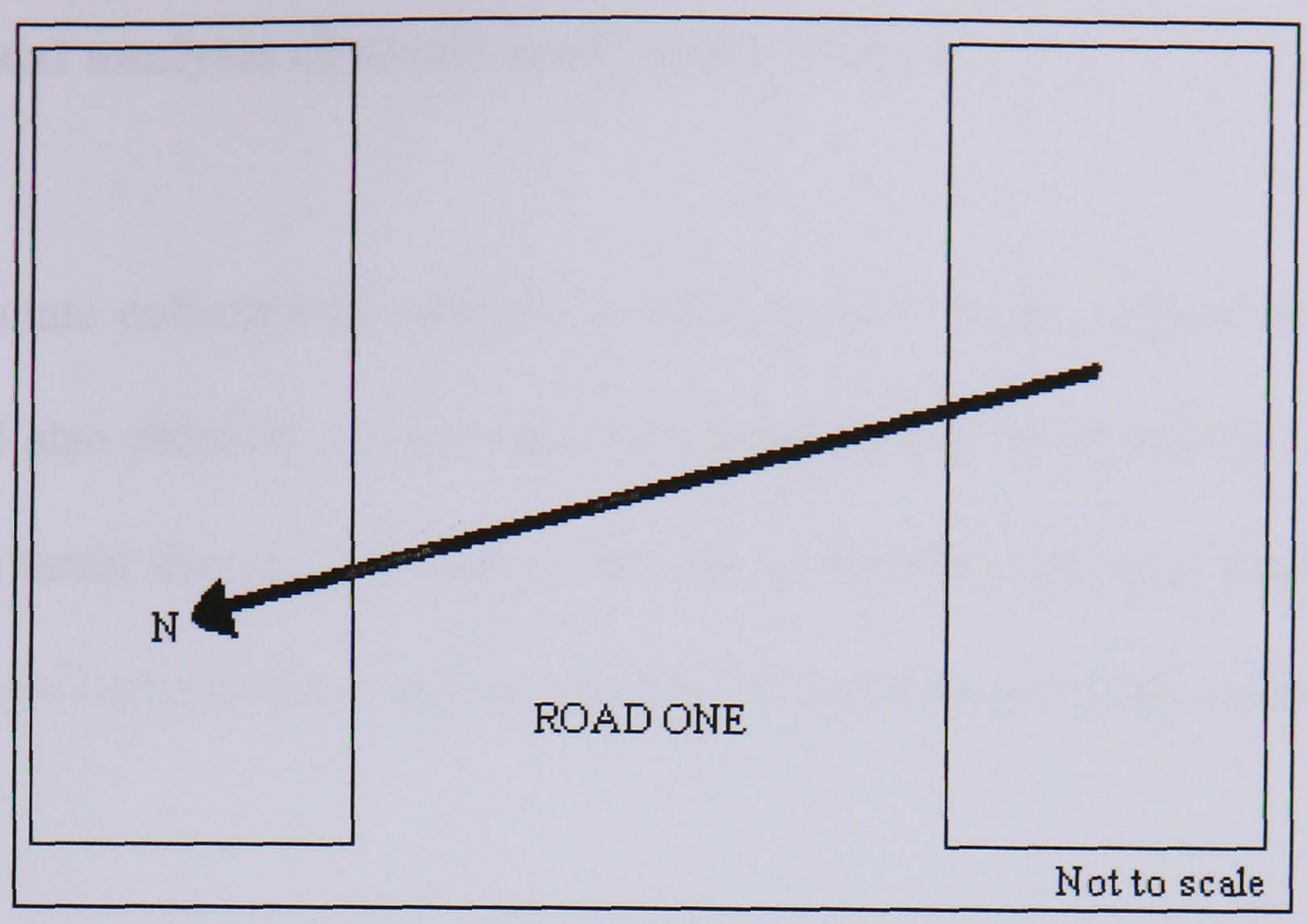


Figure 4.36: Plan view of orientation of Road One

Table 4.16: Correlation matrix of samples from with Road One (n = 57, all correlations $p < 0.001$)

	South lower	South upper	North lower	North upper
South lower	*	0.99	0.97	0.97
South upper		*	0.99	0.97
North lower			*	0.99
North upper				*

Table 4.17: Variation in respirable particulate concentrations (µg m^{-3}) from Road One during various wind directions (n = 57)

	South lower	South upper	North lower	North upper
Northerly	40	36	52	46
Easterly	25	25	23	25
Southerly	35	32	28	26
Westerly	25	23	29	26

4.11 Chemical analysis of diesel particulate matter

Diesel particulate collected as outlined in Section 3.3.7 were analysed for a variety of elements and also chloride, nitrate and sulphate to assess the possibility of identifying any chemical tracer that may be used. A loss on ignition test was also used to determine the percentage of combustible organic material. The results from this analysis are shown in Table 4.18.

The majority of diesel particulate appears to be combustible organic material, with the LOI test giving a value of 63.12% by mass being lost during combustion, of the remaining analytes sulphate constitutes the majority of total mass (19.75%). Nitrate and chloride account for 4.17% and 3.50% of total mass, respectively. Many of the elements are only present in very low concentrations with Al, Ca, Fe, K, Mg, Na, P and Zn present in significantly higher quantities than the other elements. 9.38% by mass cannot be accounted for, but is likely to comprise of organic material not combustible at 375 ° C.

Table 4.18: Chemical analysis of diesel particulate matter

Analyte	Concentration (ppm)
Al	13.49
Ca	121.51
Cd	0.089
Co	0.094
Cr	2.54
Cu	2.27
Fe	33.47
Hg	0.11
K	37.32
Li	<LOD
Mg	34.58
Mn	0.66
Mo	0.06
Na	132.56
Ni	1.35
P	44.25
Pb	0.27
Se	0.06
Sr	0.28
Ti	1.26
V	0.12
Y	0.01
Zn	27.71
Zr	0.23
Chloride	3.50 % by mass
Nitrate	4.17 % by mass
Sulphate	19.75 % by mass
LOI	63.12 % by mass
Unknown	9.38 % by mass

4.12 Dust soiling rates and settled dust analysis

Using a gravimetric method dust soiling rates in units of mg m^2 day $^{-1}$ were measured inside the main foyers of Buildings One, Two and three on a monthly basis. In the same locations and at the same time settled dust was collected for analysis by SEM and EDX. 100 individual particles were analysed each month for chemistry by EDX giving a total of 1200 analysed particles for each location over the year. Inside the three buildings 203 individual particles were analysed each month by SEM for particle size and aspect ratio, meaning 2436 particles at each location for the year were measured in this way.

4.12.1 Dust soiling rates

There is no seasonal variation in dust soiling rates inside any of the three buildings, with soiling rates being variable throughout the year (Figure 4.37). There is a noticeable peak in the soiling rate in April for Building Three, however, this is considered to be due to contamination or other interference of the monitoring slides during sample collection. The mean dust soiling rate for the entire year was greatest inside Building Two (30.51), with ANOVA suggesting this difference to be significant ($p < 0.001$). The dust soiling rate inside Buildings One (23.0) and Three (23.9) were very similar and not significantly different, even after removal of the anomalous value for April (Figure 4.38). There is an obvious relationship between the soiling rates inside Buildings One and Two, as they generally follow the same trend throughout the year. A regression analysis between the

soiling rates inside the two buildings suggest the relationship is significant ($p < 0.001$) (Figure 4.39).

Figure 4.37: Dust soiling rates inside Building One, Two and Three

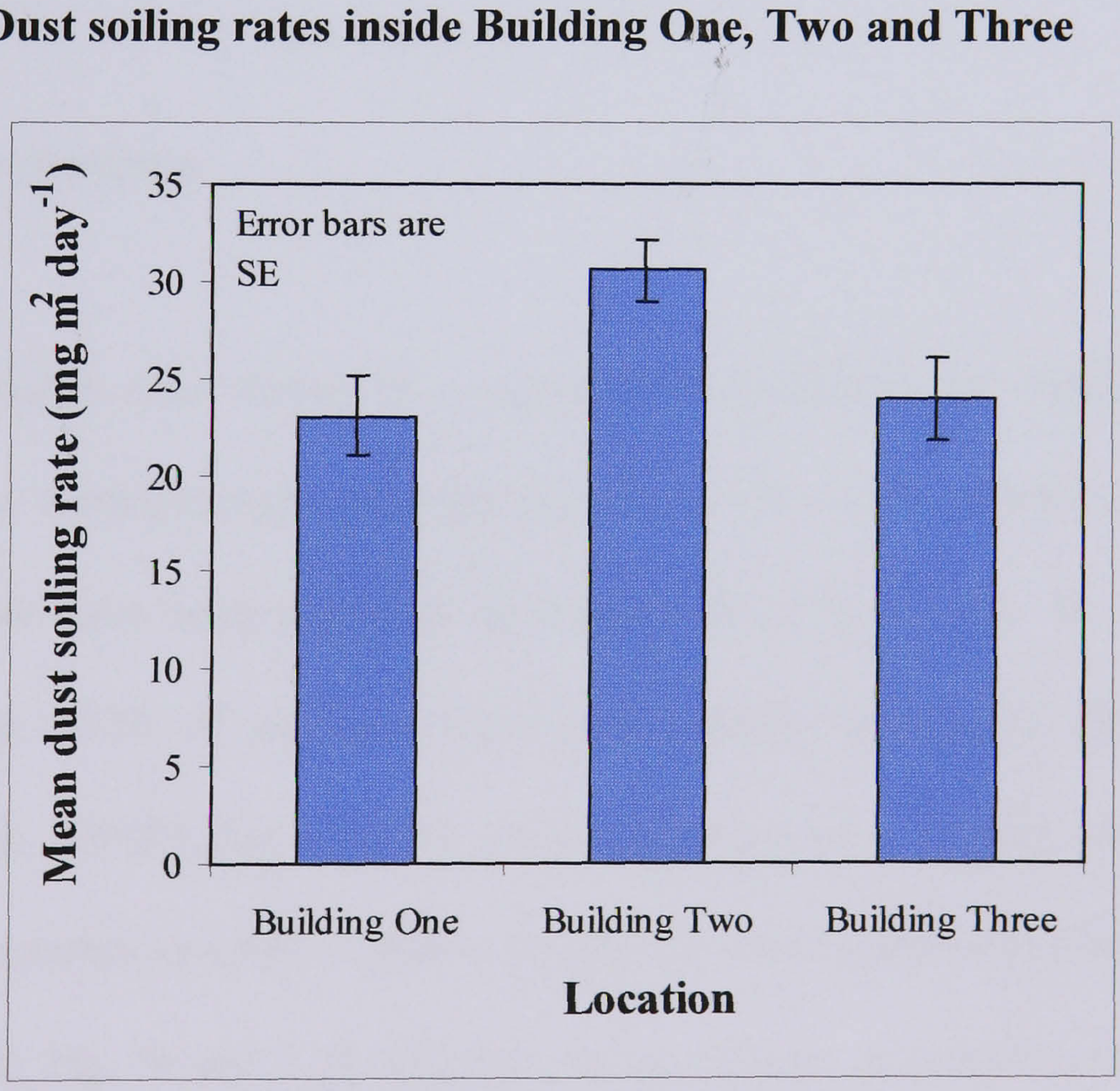


Figure 4.38: Mean dust soiling rates for the entire year of sampling

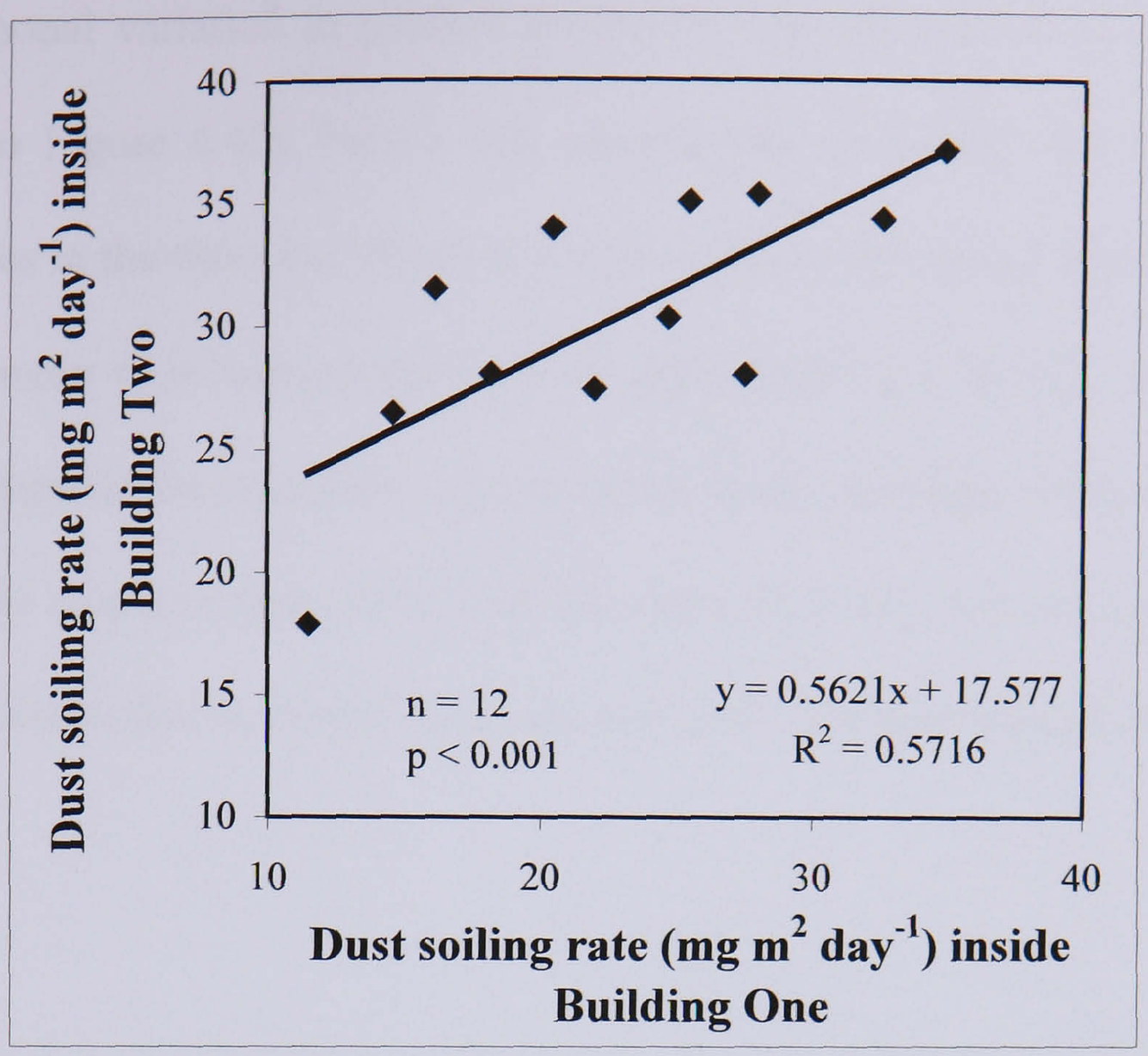


Figure 4.39: Regression analysis between soiling rates inside Buildings One and Two

4.12.2 Particle chemistry

Nineteen elements were found in concentrations sufficient for detection by EDX, however, many elements were generally present in very low quantities, often less than 10 %. Particles have been classified as being rich in Na-Cl, Ca, Si, or Si-Fe, with between 70 to 100% of particles from each sample included in these categories. Sitzmann *et al.,* (1999) also used the same categories for a similar study in London. Unclassified particles generally contained relatively equal quantities of several elements, often Cl, Fe, K, Mg, Si and S. In addition, the percentage of particles, which contained greater than 10 % S or 10 % Fe, have also been determined.

A distinct seasonal variation in particle chemistry was observed in all three buildings (Figure 4.40 to Figure 4.42). Na-Cl rich particles accounted for approximately 50 to 60% of particles in the three buildings during the winter, decreasing dramatically during spring and summer to a background level of approximately 5 to 10%. Whereas, Si-Fe rich particles showed the opposite trend in all the three buildings, rising from 5 to 20% during winter to approximately 50% in the summer. Particles rich in Ca or Si alone did not show any discernible seasonal variation and varied between 10 and 20% throughout the year.

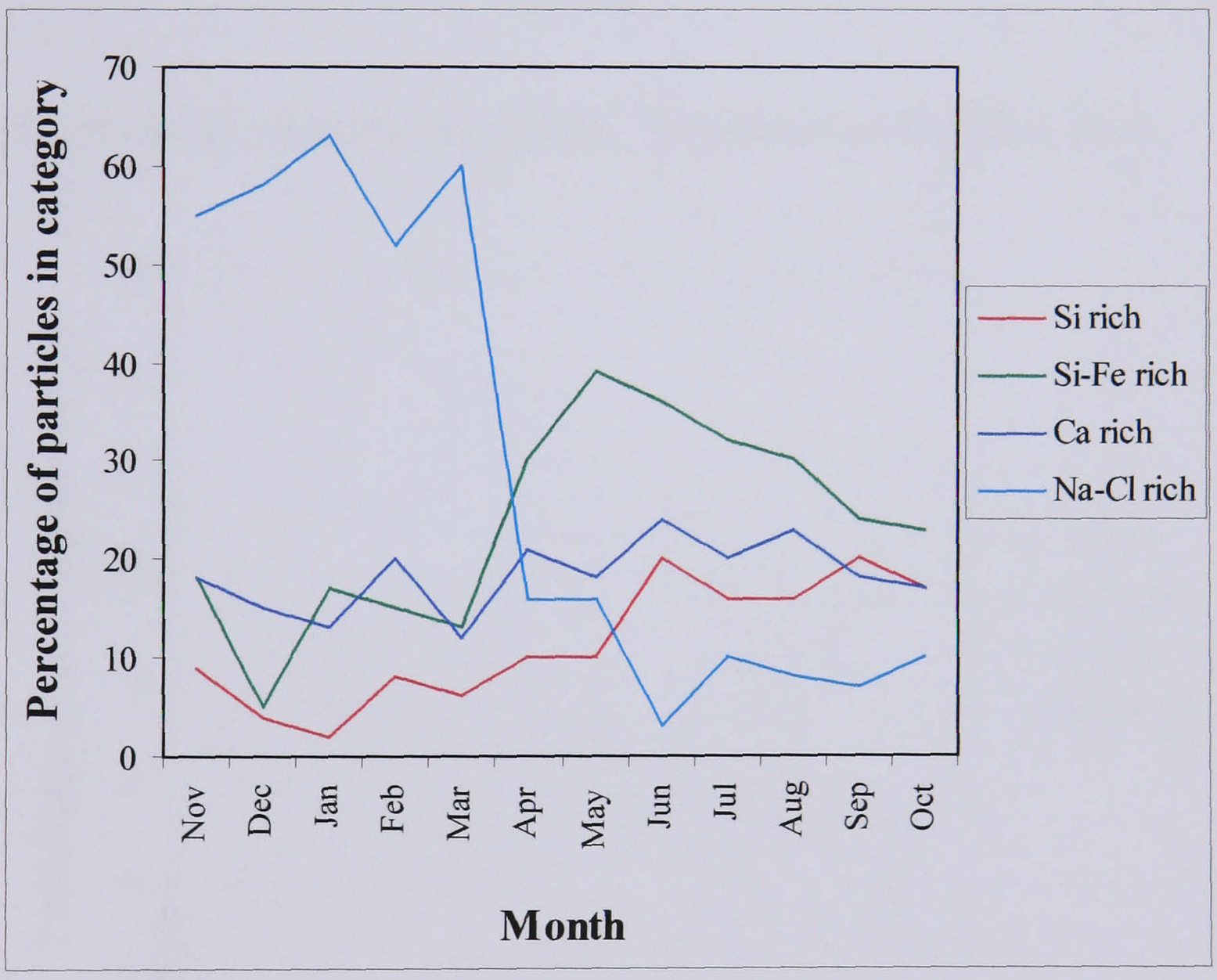


Figure 4.40: Monthly variation in particle chemistry for Building One

Figure 4.41: Monthly variation in particle chemistry for Building Two

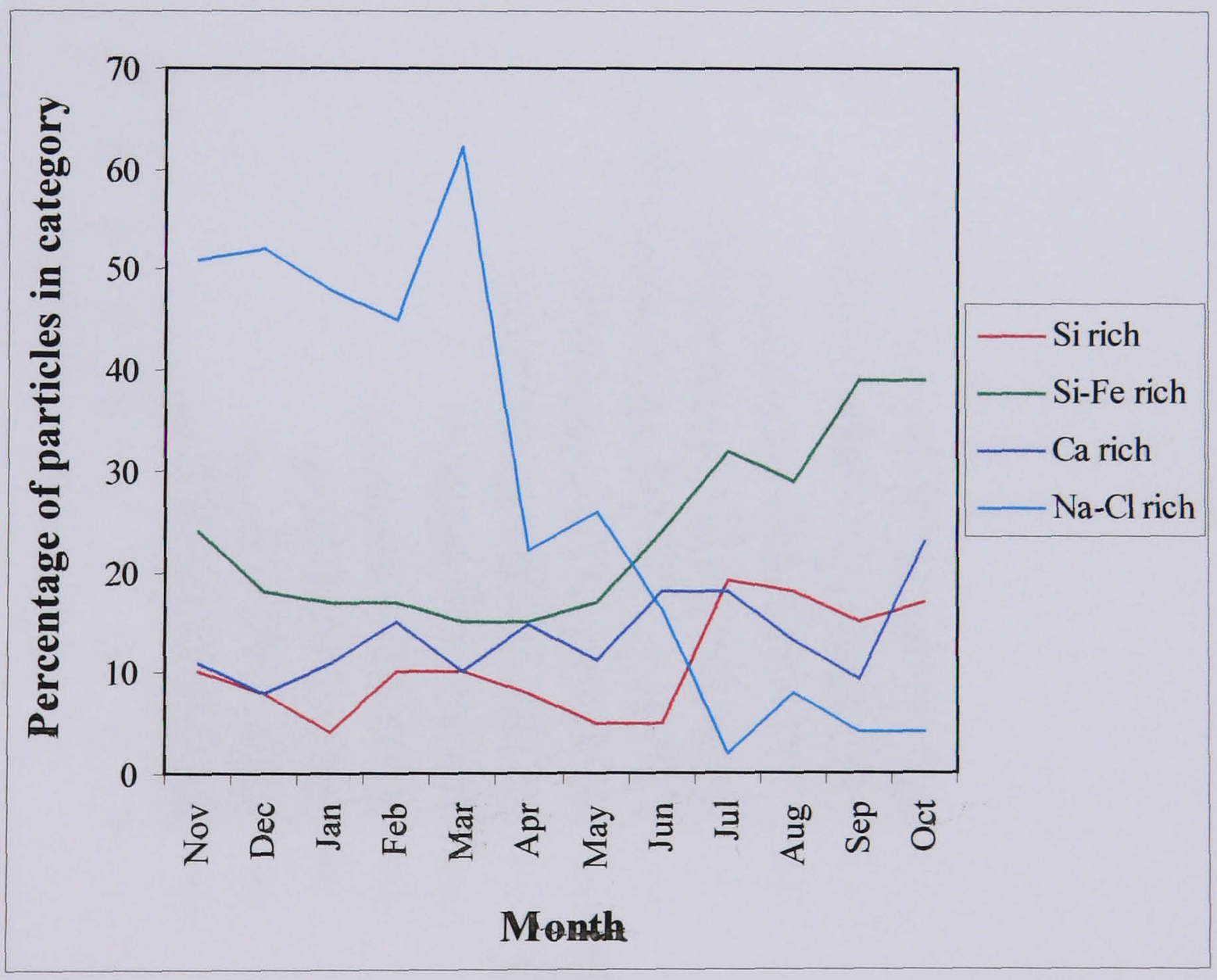


Figure 4.42: Monthly variation in particle chemistry for Building Three

A greater percentage of settled dust particles inside Buildings One and Two contained Fe and S than in Building Three (Figures 4.43 and 4.44). Inside Buildings One and Two, the average percentage of particles for the whole year containing Fe was 55 and 57%, respectively, with the average in Building Three just 38 %. The average percentage of particles containing S inside Building Three (14 %) was approximately half of those inside Buildings One (23 %) and Two (28 %).

Fe containing particles showed no seasonal variation in any of the three buildings, however, the percentage of particles containing S was greatest during the summer (Figures 4.45 to 4.47). The seasonal variation in S occurred in all three buildings, but to a lesser degree in Building Three.

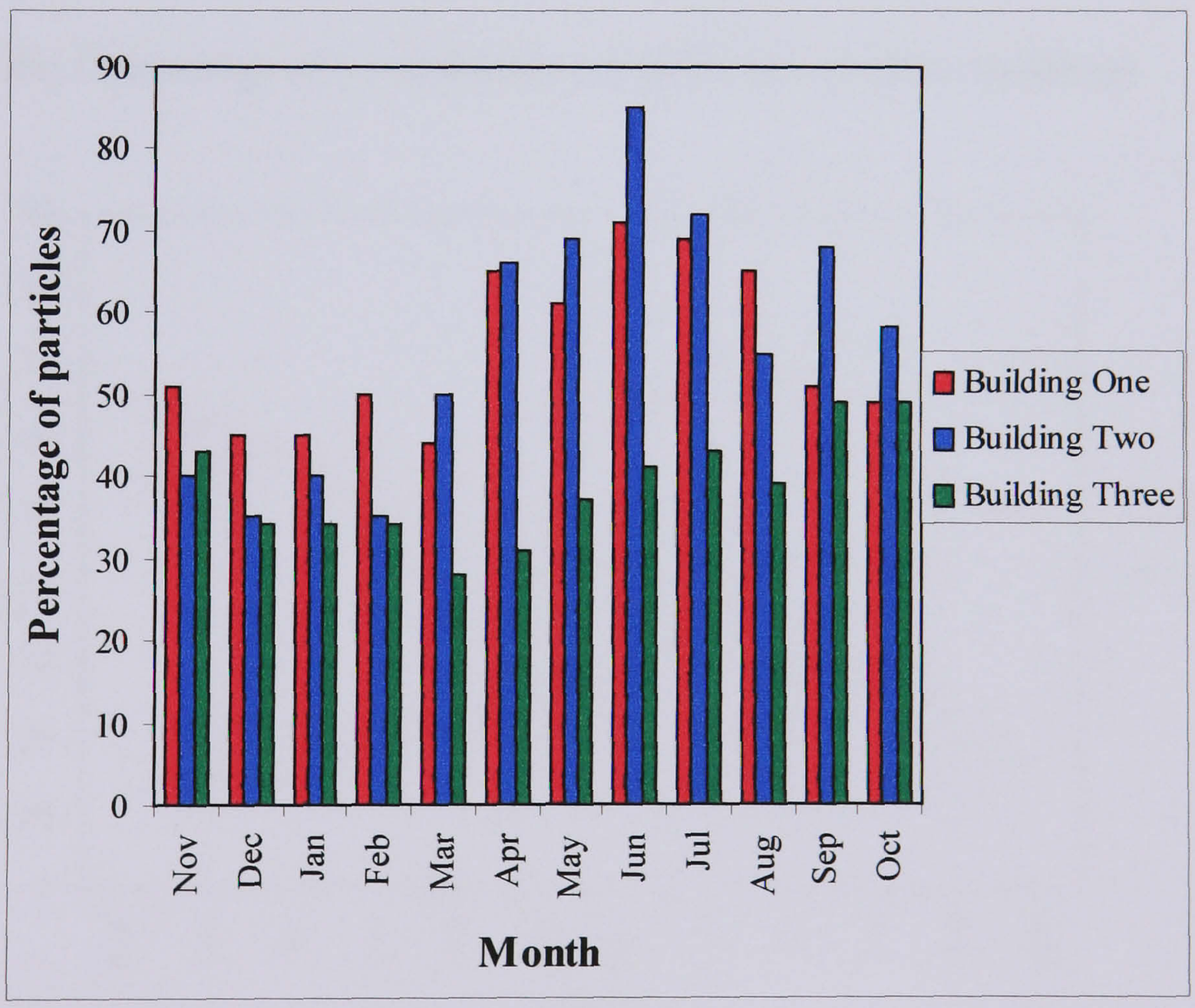


Figure 4.43: Percentage of Fe containing particles for all three buildings

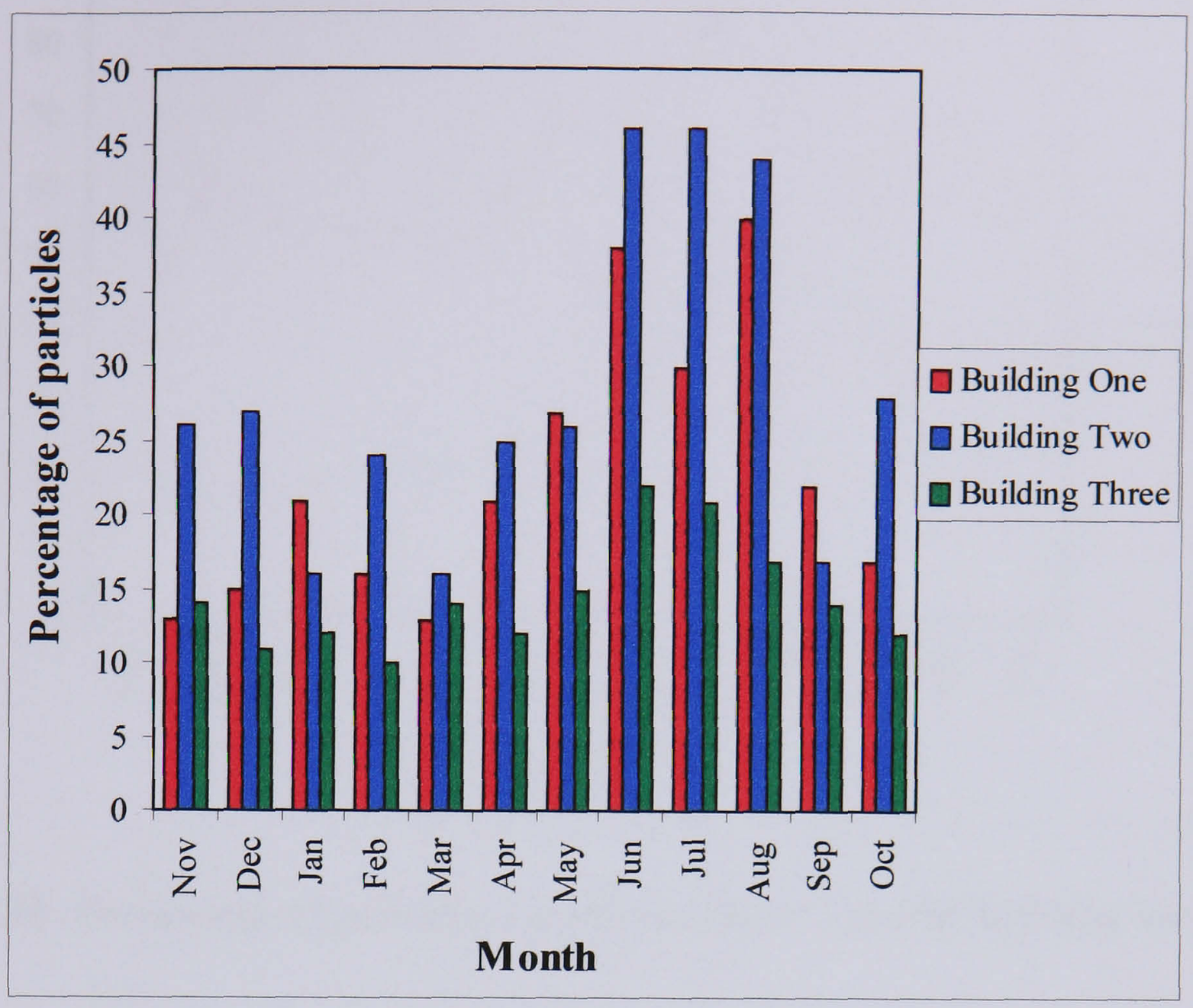


Figure 4.44: Percentage of S containing particles for all three buildings

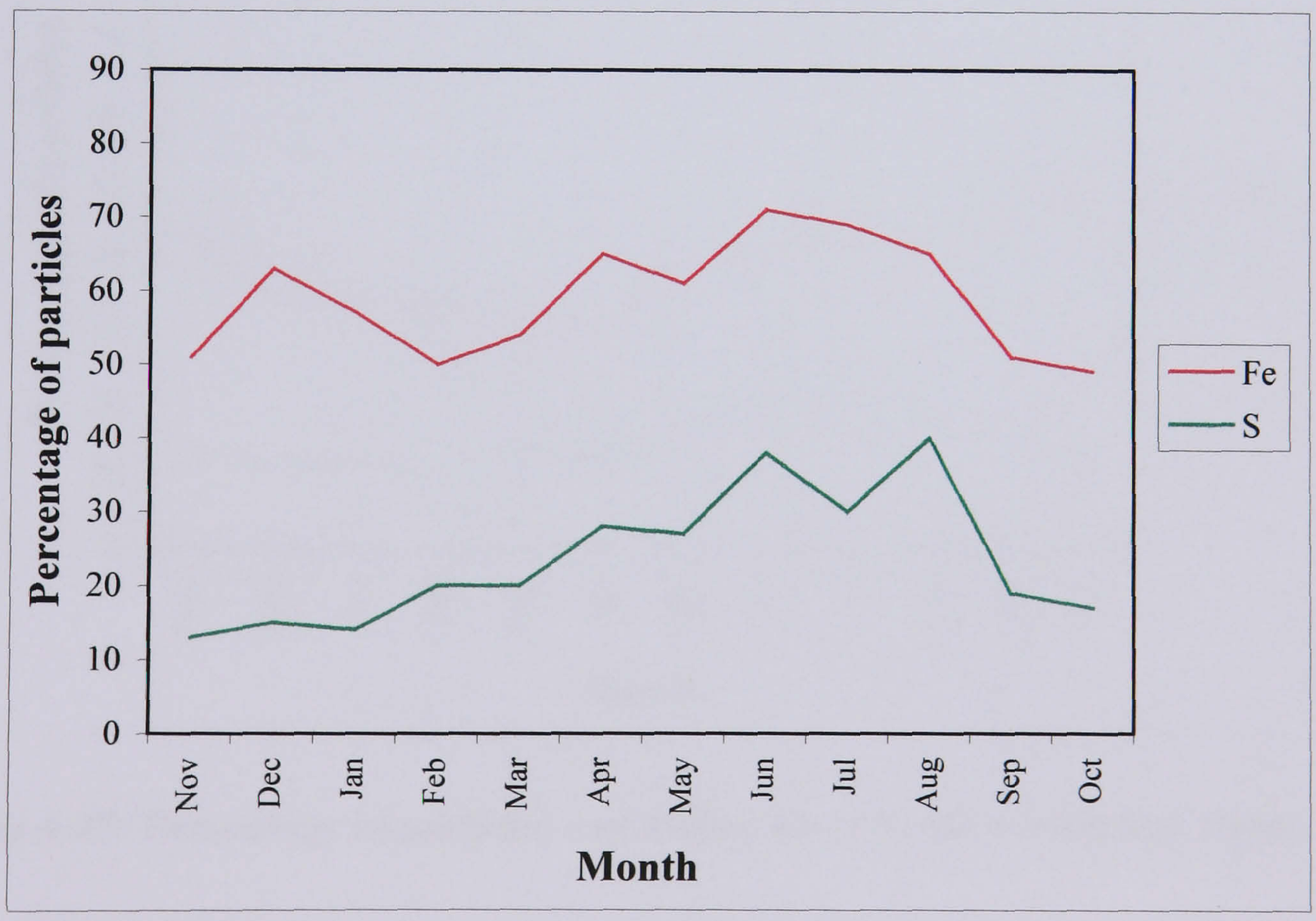


Figure 4.45: Percentage of particles containing Fe or S inside Building One

Figure 4.46: Percentage of particles containing Fe or S inside Building Two

Figure 4.47: Percentage of particles containing Fe or S inside Building Three

4.12.3 Particle morphology

Mean particle size for Building Three (5.7 μm) is noticeably larger than particles collected from Buildings One (4.9 μm) and Two (4.8 μm), where there is very little difference (Figure 4.48). For 11 months out of 12, for every sample the particle size is smaller in Buildings One and Two than for the corresponding Building Three samples (Figure 4.49). Particle size shows a seasonal variation with the average size of particle being larger during the summer months than the winter months. A *t*-test between Winter samples and Summer samples shows that the Summer/Winter difference is statistically significant for all three buildings ($p < 0.05$). There is also a significant relationship between particle size inside Building One and Building Two ($n = 12, p < 0.001, f$ ratio = 37.4) (Figure 4.50).

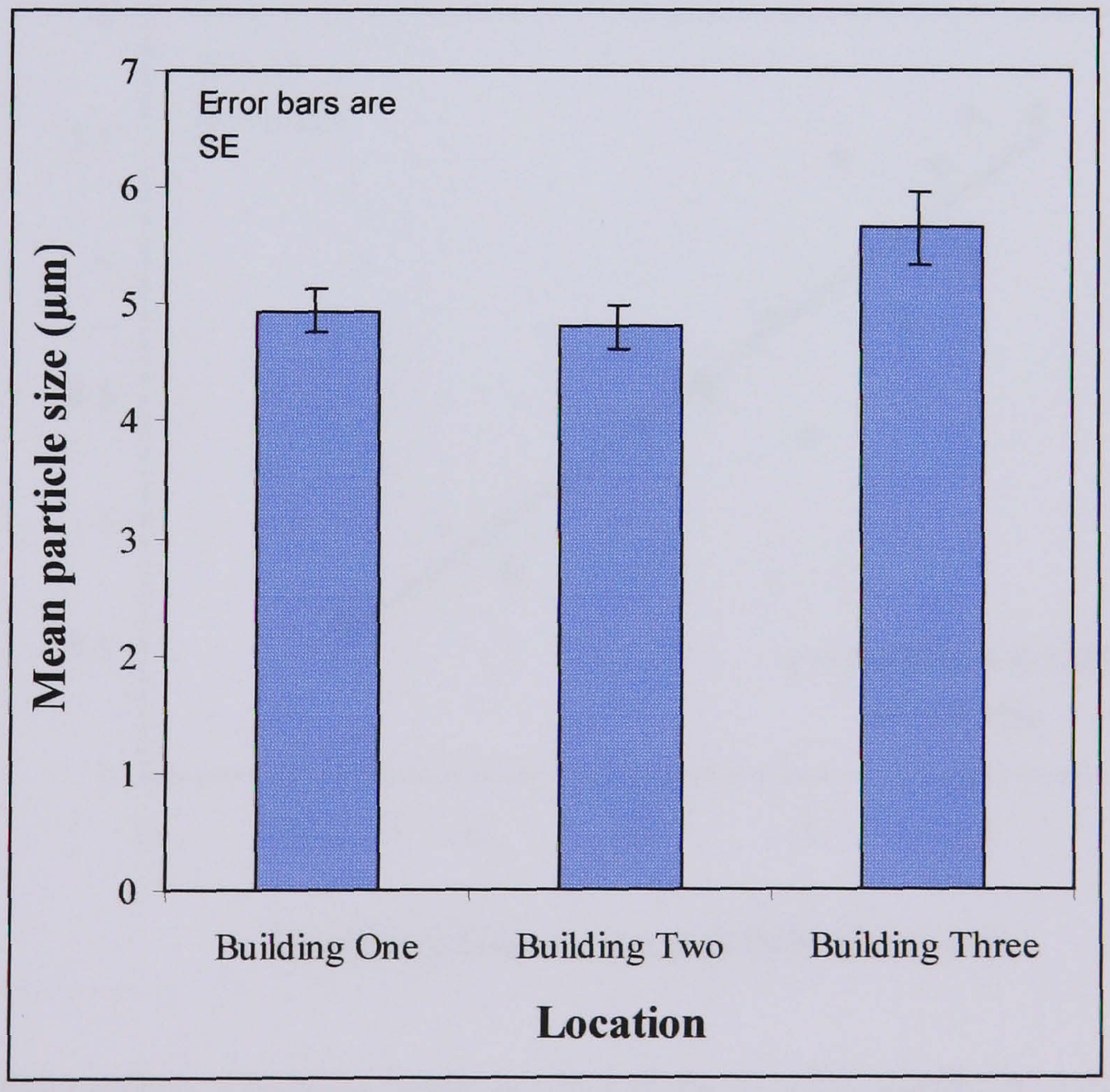


Figure 4.48: Mean particle size over the entire year for all three buildings

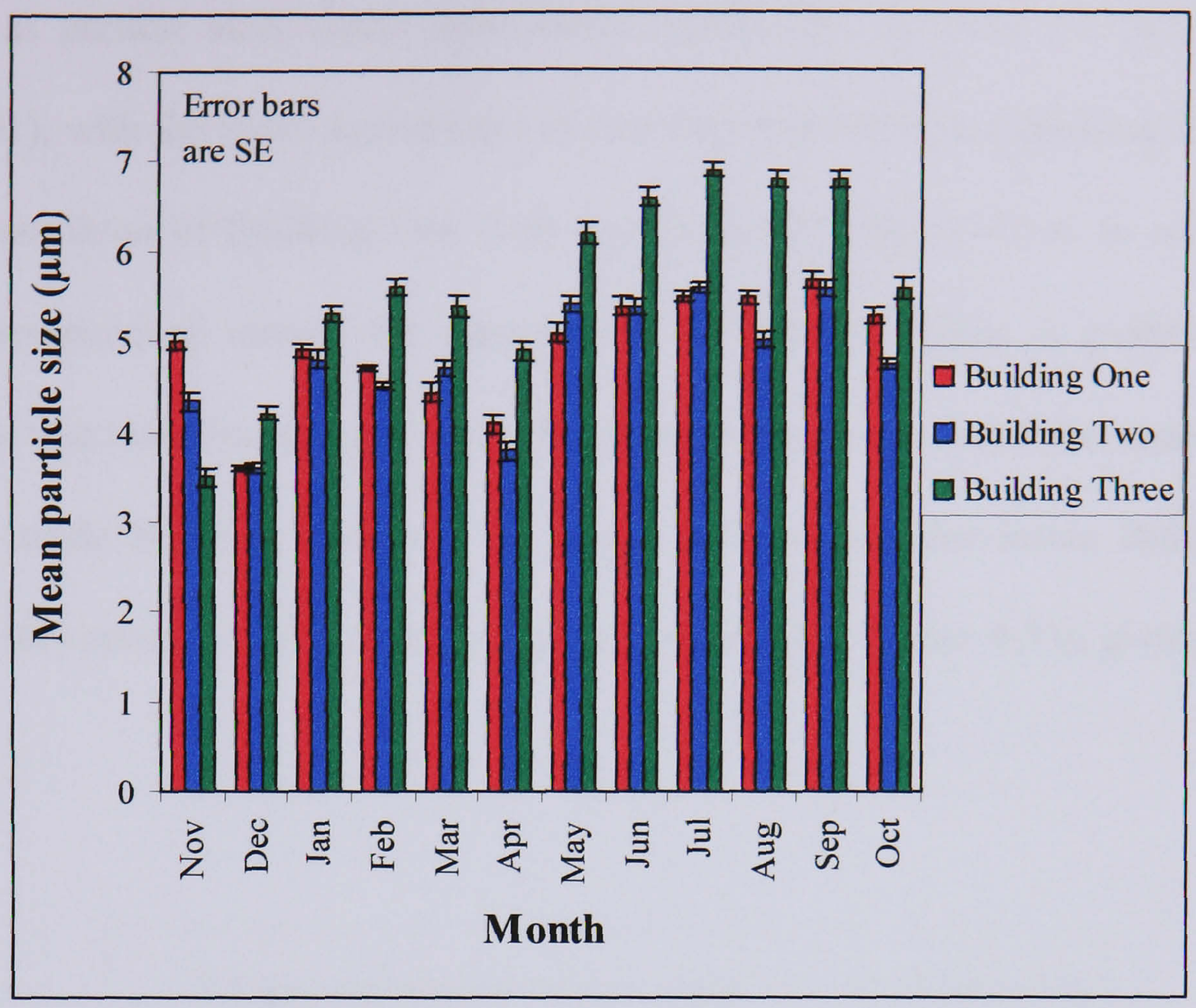


Figure 4.49: Monthly variation in particle size for all three buildings

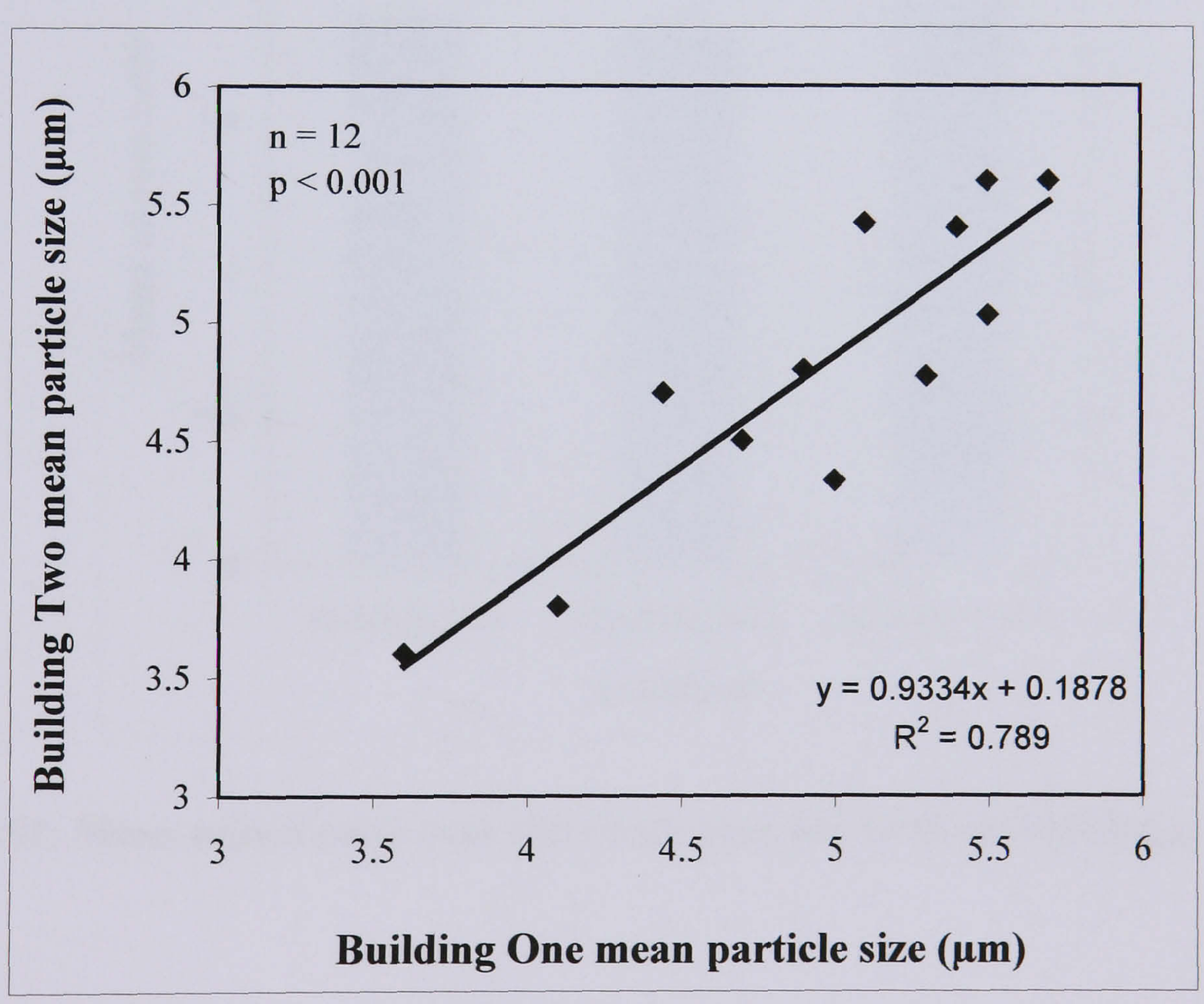


Figure 4.50: Regression analysis between particle size for Buildings One and Two

As well as particle size, aspect ratio varies significantly between the three building ($p < 0.001$), with the mean aspect ratio of particles collected from Building Three (2.1) greater than those of Building One (1.9) and Two (1.8) (Figure 4.51). In addition, for every corresponding sample the aspect ratio for Building Three is greater than for Buildings One and Two (Figure 4.52). Regression analysis between the aspect ratio of particles inside Building One with the aspect ratio of particles inside Building Two shows a very strong correlation between the two samples (Figure 4.53), giving an R^2 of 0.82.

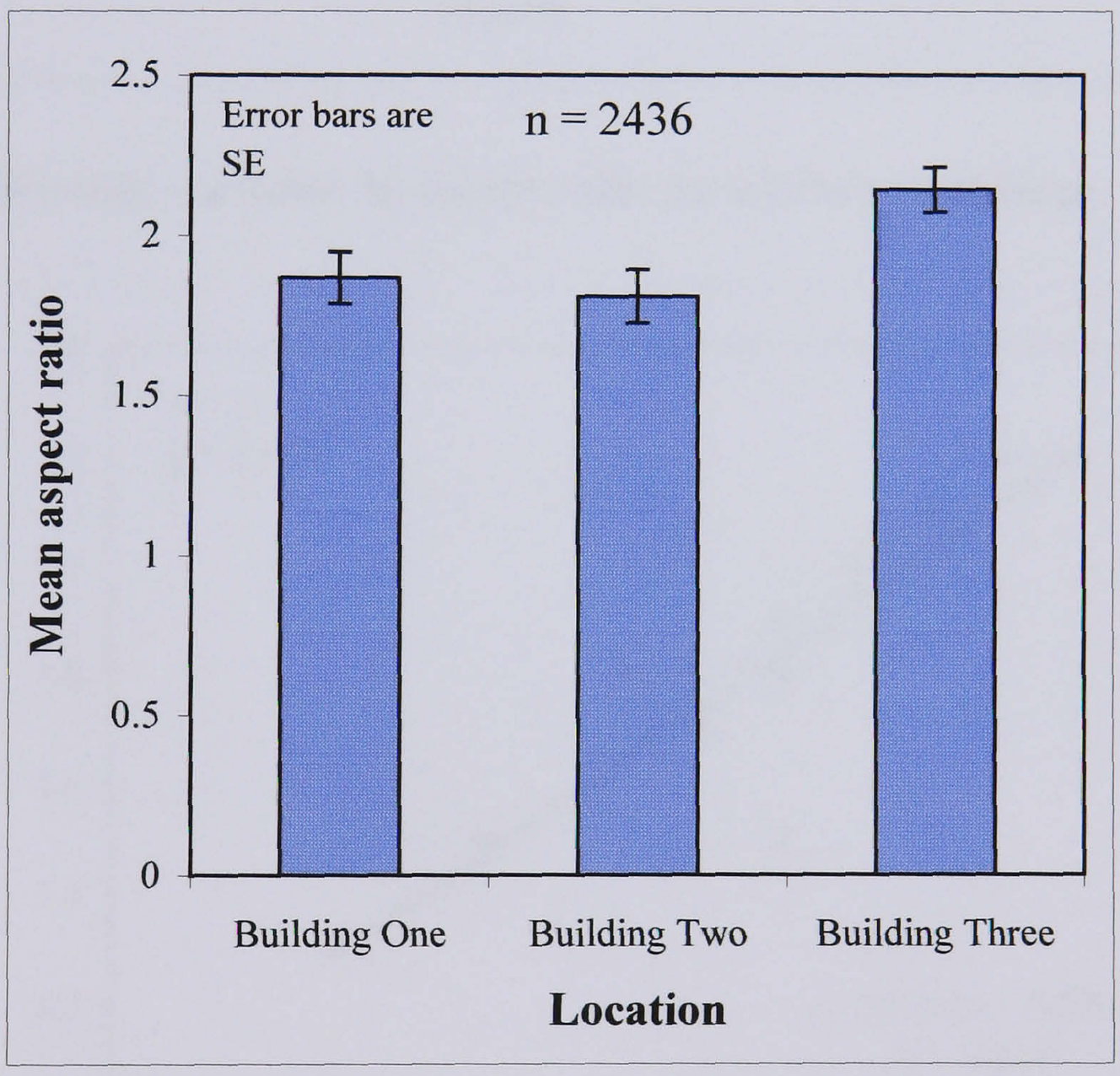


Figure 4.51: Mean aspect ratio over the entire year for all three buildings

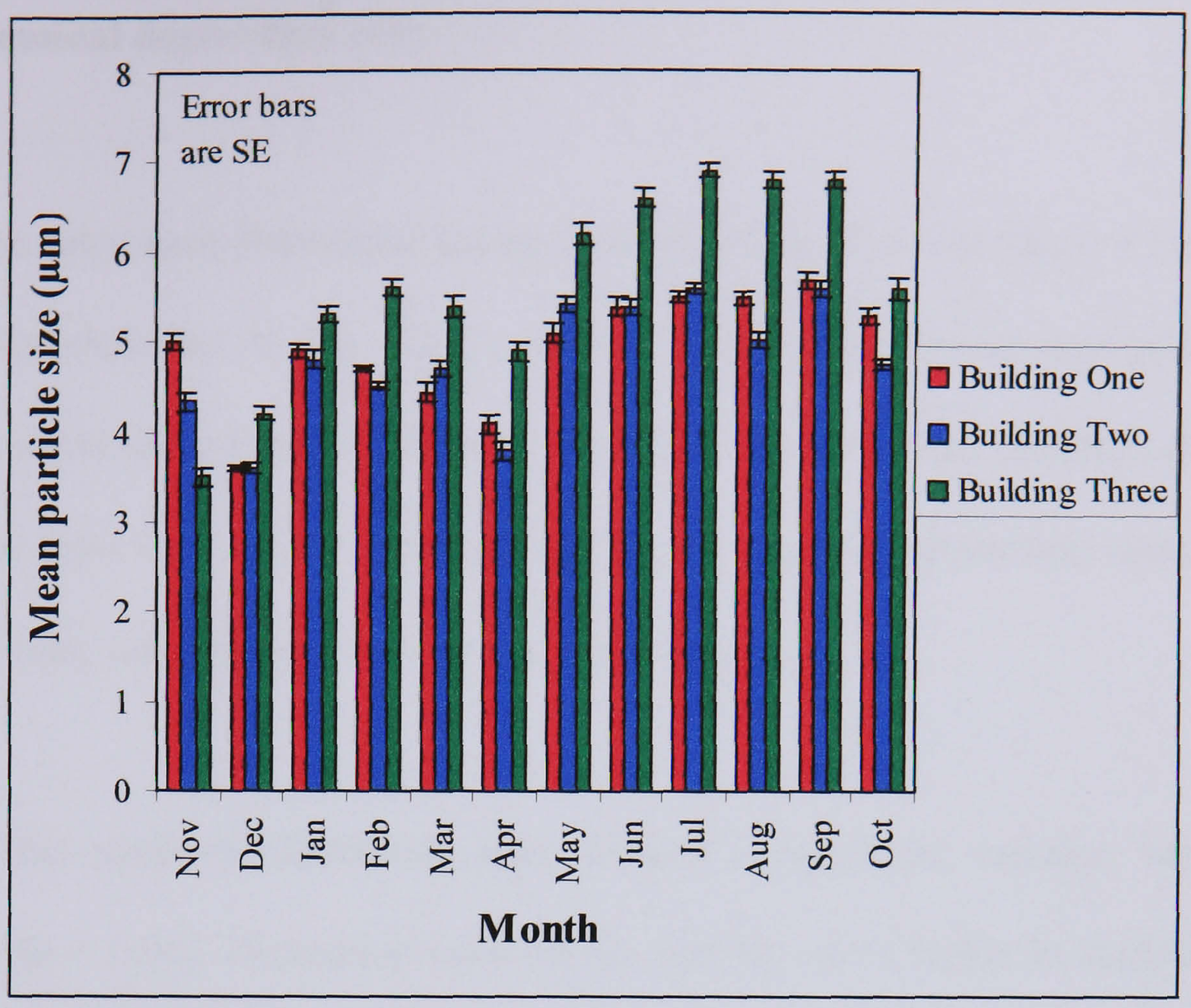


Figure 4.52: Monthly variation in aspect ratio for all three buildings

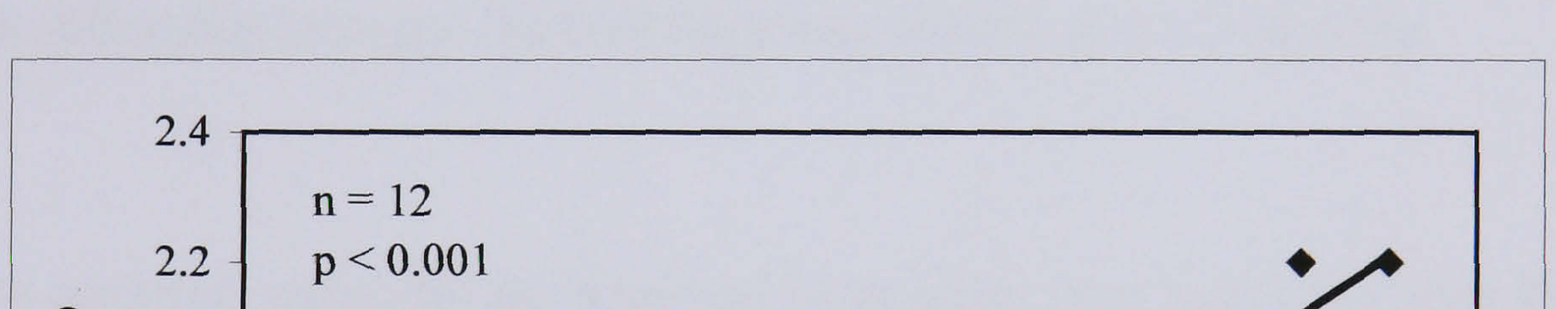


Figure 4.53: Regression analysis between aspect ratio for Buildings One and Two

4.13 Chemical deposition rate

Deposition rates were determined inside Buildings One, Two and Three for winter and summer for elements Al, Ca, Cu, Fe, K, Mg, Mn, Pb and Zn as well as the anions chloride, nitrate and sulphate (Tables 4.19 to 4.21). Inside all three buildings the greatest deposition rates were recorded for Al, Ca, Fe, K, Mg with deposition rates for these elements many times greater than for Cu, Mn, Pb and Zn.

Many of the elemental deposition rates showed a significant variation between the buildings ($p < 0.01$). Deposition rates for Ca and Mn were higher in Building Three, whereas, Cu, Fe, K, Zn and Pb were all greater in Buildings One and Two. No significant difference between the buildings was observed for Al and Mg.

Significant seasonal variations in elemental deposition rates have also been observed in all of the buildings ($p < 0.01$). Al, Ca and Pb deposition rates are lower during the summer months, whereas, K Mg and Zn are lower during winter. These seasonal variations occurred in all three buildings.

Distinct significant variations in anion deposition rates were also recorded ($p < 0.01$). Chloride deposition was significantly greater during winter and higher in Buildings One and Two. There was no significant difference between nitrate deposition between the buildings, however, during the summer months deposition of nitrate was between 50 to 100 % higher than in winter. There was no significant seasonal variation in sulphate

deposition rates, however, sulphate demonstrated the greatest difference between the buildings with deposition rates in Building Three approximately 2% of those measured in Buildings One and Two.

Table 4.19: Chemical deposition rates (μg m^2 d^{-1}) for Building One

	Winter			Summer		
	Nov	**Dec**	**Jan**	**Jun**	**Jul**	**Aug**
Al	320	332	358	459	416	444
Ca	279	287	306	424	384	365
Cu	11.3	10.7	9.9	8.6	9.1	8.8
Fe	709	880	759	780	794	759
K	171	187	168	147	156	159
Mg	103	110	110	89	94	98
Mn	15.6	16.3	16.2	17.4	17.6	16.4
Pb	13.6	14.2	14.2	10.7	11.0	11.7
Zn	25.5	23.6	26.0	16.3	17.9	16.2
Chloride	228	558	525	231	157	90
Nitrate	15.5	16.8	16.9	28.4	30.3	28.8
Sulphate	855	874	863	987	897	846

Table 4.20: Chemical deposition rates (μg m^2 d^{-1}) for Building Two

	Winter			Summer		
	Nov	**Dec**	**Jan**	**Jun**	**Jul**	**Aug**
Al	279	263	240	376	357	347
Ca	328	329	344	458	414	430
Cu	16.0	15.9	15.3	7.9	7.8	8.0
Fe	758	788	776	718	677	659
K	169	161	170	139	129	124
Mg	150	164	156	123	111	113
Mn	19.2	20.7	21.2	25.7	23.3	29.7
Pb	18.4	17.0	17.7	13.3	13.4	13.1
Zn	30.1	29.8	28.6	16.7	17.0	18.0
Chloride	206	742	718	103	93	134
Nitrate	26.0	25.3	25.0	35.0	35.6	44.9
Sulphate	1333	1001	1271	1182	1262	1286

Table 4.21: Chemical deposition rates (μg m^{-2} d^{-1}) for Building Three

	Winter			Summer		
	Nov	**Dec**	**Jan**	**Jun**	**Jul**	**Aug**
Al	306	627	304	408	426	418
Ca	528	539	557	662	606	630
Cu	9.1	9.8	10.3	7.2	6.7	6.7
Fe	509	517	485	450	481	488
K	84	84	83	49	45	49
Mg	125	114	124	99	79	89
Mn	43.2	37.7	34.3	41.3	42.4	49.7
Pb	8.5	9.1	9.0	7.4	6.7	7.0
Zn	12.6	17.9	15.8	6.0	6.4	2.4
Chloride	173	158	157	9.2	10.0	9.6
Nitrate	10.3	9.4	8.5	21.4	31.6	30.9
Sulphate	25.2	25.7	27.1	27.7	23.3	25.3

4.14 Street dust and indoor dust analysis

Street dust and indoor dust samples were collected once a month for one year and following size fractionation and conditioning were analysed for trace elements and the major anions. The magnetic properties of the dust were also determined.

4.14.1 Street dust and indoor dust chemistry

4.14.1.1 Seasonal variation

To assess any variation in street dust and indoor dust chemistry, the monthly concentration of analytes for all particles smaller than 250 μm were determined for each road (Tables 4.22 to 4.24) and for each building (Tables 4.25 to 4.28). Chloride is the only analyte to show any discernible seasonal variation, showing an increase of

approximately 250 to 400 % in winter for all roads, when comparing summer and autumn concentrations. All of the other analytes vary erratically or show very little variation. The same trend is seen in indoor dust chemistry, with chloride also being the only analyte to display a seasonal variation, with a winter increase of a similar magnitude in all four buildings.

Table 4.22: Monthly variation in dust chemistry for Road One

	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Jan	Feb	Mar	Apr
Al	314	296	304	302	293	290	308	341	312	273	313	303
Ca	156	283	244	243	243	255	279	169	243	249	319	200
Cu	12.3	15.8	19.8	24.2	26.6	20.4	15.9	16.4	15.6	18.6	16.6	18.2
Fe	315	256	390	584	485	353	260	350	240	354	376	338
K	121	116	119	89.3	104	78.5	100	80.6	111	76.7	97.7	96.9
Mg	56.2	53.7	55.4	62.1	57.4	60.4	55.5	60.7	62.6	55.8	69.9	58.1
Mn	31.7	22.4	24.1	24.4	18.0	26.3	28.1	21.8	19.3	15.3	18.9	22.6
Pb	28.2	22.7	23.6	23.2	16.3	21.4	25.5	26.7	18.8	15.8	18.3	18.3
Zn	32.6	27.0	38.4	48.6	43.7	35.3	30.1	30.0	28.4	31.2	32.8	30.2
Sulphate	375	440	375	359	319	355	393	423	336	295	446	457
Nitrate	11.5	8.3	22.9	18.2	10.0	11.2	8.9	8.9	10.2	9.3	10.1	11.4
Chloride	38.6	44.2	40.0	42.8	44.4	42.6	44.0	208	222	241	141	89.4
LOI	31.3	36.7	34.8	36.9	35.0	34.3	34.1	38.0	36.3	34.1	35.1	31.8
All concentrations in $\mu g\ g^{-1}$, organics expressed as a percentage of mass.												

Table 4.23: Monthly variation in dust chemistry for Road Two

	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Jan	Feb	Mar	Apr
Al	1019	845	815	997	903	899	968	963	1036	864	1172	1093
Ca	367	340	353	333	313	341	368	292	324	308	358	318
Cu	7.0	7.3	6.0	5.5	8.8	7.4	6.0	7.1	5.6	7.9	5.0	6.9
Fe	148	228	225	188	252	336	214	322	258	251	330	294
K	358	248	210	247	179	200	255	194	213	162	322	293
Mg	40.6	54.4	61.9	45.4	38.2	37.2	44.8	64.8	56.0	44.6	53.7	54.3
Mn	70.9	58.4	49.5	65.6	74.7	62.0	66.9	54.3	40.3	53.2	56.3	42.1
Pb	26.7	28.2	20.6	22.9	21.3	29.4	21.0	19.3	25.7	19.7	21.6	27.7
Zn	11.7	7.9	9.8	7.5	12.0	9.9	9.9	10.1	9.2	9.6	10.8	10.8
Sulphate	14.4	15.0	16.0	15.0	18.2	15.8	14.3	16.8	14.9	14.9	18.0	15.7
Nitrate	9.7	10.4	12.8	14.9	9.7	7.5	9.5	10.6	9.1	11.2	8.0	10.4
Chloride	30.3	28.0	25.1	24.3	27.8	25.6	26.0	257	270	249	138	73.1
LOI	15.2	13.5	14.4	14.0	13.0	13.1	14.5	12.0	13.7	15.0	13.2	15.1
All concentrations in $\mu g\ g^{-1}$, organics expressed as a percentage of mass.												

Table 4.24: Monthly variation in dust chemistry for Road Three

	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Jan	Feb	Mar	Apr
Al	408	635	625	475	534	399	469	576	551	693	725	599
Ca	1224	1224	1216	1234	1060	1224	1130	1111	1083	1269	1253	1075
Cu	3.2	3.8	3.8	3.3	3.5	4.1	3.9	3.4	4.0	4.2	3.3	4.6
Fe	408	333	332	311	277	158	235	251	330	270	291	219
K	55.1	189	195	94.7	147	104	150	109	114	169	190	149
Mg	40.8	40.2	32.1	20.9	29.5	31.9	26.5	31.3	23.4	31.2	18.7	27.6
Mn	23.5	44.9	48.6	33.6	27.1	23.7	33.8	35.1	19.7	34.2	40.0	37.0
Pb	10.9	11.7	10.3	6.0	15.5	3.9	8.3	15.1	11.3	10.5	7.1	4.9
Zn	8.7	13.1	13.9	9.5	11.4	12.4	13.0	12.3	11.5	14.2	10.7	9.9
Sulphate	12.4	11.9	12.8	10.0	13.4	12.4	12.4	11.5	11.6	11.7	13.5	11.1
Nitrate	8.0	5.9	12.8	11.5	6.4	6.7	7.7	5.9	7.1	6.2	6.5	5.5
Chloride	22.6	27.7	23.4	24.3	26.8	24.3	29.1	169.8	161.0	141.5	109	59.7
LOI	12.5	22.3	20.2	21.5	17.9	20.7	21.6	19.8	20.3	21.7	24.3	24.6
All concentrations in $\mu g\ g^{-1}$, organics expressed as a percentage of mass.												

Table 4.25: Monthly variation in dust chemistry for Building One

	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Jan	Feb	Mar	Apr
Al	448	394	447	402	460	409	453	452	435	370	459	413
Ca	235	455	394	371	367	384	428	269	408	381	497	324
Cu	5.6	8.1	9.0	12.6	13.4	10.3	8.3	8.6	8.2	8.3	8.1	10.0
Fe	287	234	257	452	388	253	143	290	180	236	273	247
K	158	163	173	125	146	111	124	109	156	109	137	146
Mg	49.5	41.1	33.5	50.4	39.6	51.8	37.6	48.5	42.6	34.7	46.5	42.2
Mn	41.6	32.5	36.1	33.1	25.1	38.3	42.7	29.7	26.2	21.0	28.2	32.1
Pb	18.0	17.5	16.3	16.4	11.8	16.0	17.3	18.0	11.9	12.2	14.3	14.3
Zn	16.1	14.6	21.3	25.5	21.2	17.2	15.7	14.6	15.1	17.3	16.8	14.9
Sulphate	162	165	140	129	124	106	138	152	120	103	139	176
Nitrate	9.0	7.0	20.2	17.4	9.3	9.9	7.7	8.7	7.3	8.0	9.0	9.5
Chloride	44.0	54.1	41.8	43.8	53.1	55.2	54.5	259	258	281	168	105
LOI	17.2	22.5	22.4	22.4	18.9	21.8	21.6	19.7	25.4	21.9	19.6	18.4
All concentrations in $\mu g\ g^{-1}$, organics expressed as a percentage of mass.												

Table 4.26: Monthly variation in dust chemistry for Building Two

	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Jan	Feb	Mar	Apr
Al	469	405	427	407	432	440	422	493	459	394	464	389
Ca	253	500	414	405	397	376	408	282	395	387	481	330
Cu	6.5	8.6	11.3	12.5	14.4	10.0	8.9	8.6	8.1	9.1	9.4	10.2
Fe	292	219	269	461	383	229	138	284	193	248	291	266
K	170	159	178	133	139	120	131	121	168	110	132	139
Mg	46.9	39.2	42.2	58.1	44.5	49.4	41.9	49.2	49.0	37.4	52.3	39.3
Mn	45.0	33.5	36.4	35.0	27.0	39.4	42.2	31.8	25.9	22.6	28.2	32.9
Pb	19.0	19.1	18.4	16.5	11.5	16.4	18.4	20.2	13.6	11.8	12.9	14.5
Zn	16.2	14.5	21.3	23.3	22.8	16.6	15.2	16.1	14.7	18.3	18.3	15.5
Sulphate	167	179	146	139	119	116	152	149	117	95.6	153	167
Nitrate	9.7	7.3	20.4	18.0	10.0	10.1	8.0	8.0	8.1	7.7	9.3	10.6
Chloride	46.0	54.3	48.2	51.1	53.8	50.6	59.1	258	242	311	165	96.8
LOI	18.6	23.7	20.2	20.3	20.8	22.8	21.4	19.2	24.0	23.7	19.2	17.9
All concentrations in $\mu g\ g^{-1}$, organics expressed as a percentage of mass.												

Table 4.27: Monthly variation in dust chemistry for Building Three

	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Jan	Feb	Mar	Apr
Al	976	759	747	977	831	784	869	957	945	826	1025	1095
Ca	286	307	315	255	246	279	320	242	278	265	289	252
Cu	5.7	6.3	4.3	4.2	7.2	6.5	4.9	5.6	5.2	6.6	3.7	5.6
Fe	137	201	180	180	253	297	194	297	234	219	311	255
K	321	253	200.5	220	155	187	233	192	188	150	281	278
Mg	40.3	48.5	52.7	44.0	35.1	32.4	41.0	56.8	50.6	39.9	47.0	48.3
Mn	64.6	53.8	43.1	63.5	67.6	56.7	65.5	51.8	36.2	46.3	52.7	39.0
Pb	22.9	26.3	18.3	20.4	18.1	29.0	19.7	17.2	22.5	16.8	19.2	26.2
Zn	9.0	6.3	7.6	5.3	9.3	7.9	8.0	7.8	7.4	6.9	8.2	8.4
Sulphate	12.0	13.7	14.3	13.7	15.8	13.6	13.2	13.5	13.7	13.7	15.7	12.8
Nitrate	13.8	15.8	17.8	18.1	15.3	13.2	16.4	15.6	15.2	17.0	14.9	14.7
Chloride	26.6	24.5	21.7	22.1	22.8	24.3	23	201	217.4	212.2	119.3	66.6
LOI	11.3	10.1	10.1	10.3	10.7	9.9	10.9	32.2	34.0	46.7	27.9	17.4
All concentrations in $\mu g\ g^{-1}$, organics expressed as a percentage of mass.												

Table 4.28: Monthly variation in dust chemistry for Building Four

	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Jan	Feb	Mar	Apr
Al	382	611	597	477	505	380	419	552	505	648	692	590
Ca	1219	1152	1161	1171	1071	1180	1080	1126	1040	1247	1187	975
Cu	2.7	3.4	3.1	2.9	3.1	3.6	3.4	2.9	3.7	3.7	3.1	4.3
Fe	403	303	310	293	276	134	212	235	317	237	280	200
K	50.5	192	187	89.9	149	100	148	106	107	173	196	140
Mg	36.6	39.5	32.1	17.5	26.9	29.6	25.8	30.6	21.6	29.2	18.8	27.2
Mn	22.2	41.6	45.0	32.7	26.5	22.6	31.5	33.7	18.6	33.0	37.2	36.9
Pb	10.5	10.7	9.5	5.5	15.2	3.7	7.6	13.9	11.0	10.0	6.9	4.4
Zn	8.3	12.1	12.9	8.8	9.7	11.5	12.2	11.1	10.9	12.7	10.7	9.4
Sulphate	10.5	9.4	10.9	9.1	12.2	11.3	9.9	9.7	10.3	10.7	11.5	10.1
Nitrate	12.7	10.0	16.4	14.1	12.	11.2	11.6	10.2	11.1	11.2	11.4	9.9
Chloride	19.3	23.7	21.9	21.2	21.2	21.0	25.0	134	123	114	94.4	45.7
LOI	13.7	21.6	19.8	20.8	17.2	19.5	20.7	38.1	43.0	40.1	33.5	26.5
All concentrations in $\mu g\ g^{-1}$, organics expressed as a percentage of mass.												

4.14.1.2 Variation between Roads

Street dust chemistry, for particles smaller than 250 μm, varies significantly between each of the roads (Table 4.29). The largest variation for any of the elements is observed for Ca, with dust from Road Three, containing almost 400% more Ca than either Road One or Road Two. The greatest difference for any of the analytes is seen for sulphate, where concentrations at Road One are an order of magnitude greater than at Roads Two and Three. Interestingly, other analytes that may be associated with traffic emissions are also greater at Road One, for example, Zn and Cu concentrations are over twice as high.

Table 4.29: Mean analyte concentrations (μg g^{-1}) for all three roads

	Road One	Road Two	Road Three
Al	467.00	959.04	564.02
Ca	382.97	330.78	1174.19
Cu	11.73	6.65	3.80
Fe	313.29	260.66	281.43
K	149.96	233.57	145.40
Mg	50.71	50.25	28.93
Mn	34.53	58.22	33.51
Pb	17.78	23.75	9.42
Zn	21.48	9.81	12.09
Sulphate	152.24	15.85	12.05
Nitrate	11.71	10.25	7.44
Chloride	132.53	97.69	68.59
LOI %	19.18	13.75	20.83

4.14.1.3 Variation between buildings

Concentrations inside Buildings One and Two are almost identical, however, concentrations for Building Two are slightly greater for most of the analytes (Table

4.30). The traffic related analytes Zn, Cu and sulphate are all noticeably greater inside Buildings One and Two, with sulphate an order of magnitude larger. A large difference is also observed for Ca, being approximately 500% greater inside Building Four, when compared to the other three buildings.

Table 4.30: Mean analyte concentrations between all four buildings

	Building One	Building Two	Building Three	Building Four
Al	428.44 (8.7)	433.54 (9.4)	899.33 (32.4)	530.29 (29.7)
Ca	375.98 (21.7)	385.80 (20.5)	277.88 (7.7)	1134.57 (22.7)
Cu	9.21 (0.6)	9.79 (0.6)	5.49 (0.3)	3.34 (0.1)
Fe	269.95 (23.9)	272.78 (24.4)	229.81 (15.8)	267.08 (19.9)
K	137.96 (6.5)	141.73 (6.3)	221.62 (15.3)	136.89 (13.4)
Mg	43.16 (1.8)	45.80 (1.8)	44.72 (2.1)	27.95 (1.9)
Mn	32.23 (1.9)	33.32 (2.0)	53.41 (3.1)	31.79 (2.3)
Pb	15.34 (0.7)	16.02 (0.9)	21.39 (1.2)	9.07 (1.0)
Zn	17.52 (1.0)	17.74 (0.9)	7.67 (0.3)	10.85 (0.4)
Sulphate	137.72 (6.0)	141.63 (7.2)	13.80 (0.3)	10.46 (0.3)
Nitrate	10.26 (1.2)	10.60 (1.2)	9.50 (0.4)	7.28 (0.5)
Chloride	118.12 (27.8)	119.63 (28.3)	91.90 (23.8)	64.24 (13.5)
% Organics	20.98 (0.7)	20.99 (0.6)	15.45 (3.6)	21.40 (2.9)
$\mu g\ g^{-1}$ (Standard error shown in parenthesis)				

4.14.1.4 Indoor and outdoor relationships

To assess the variation between indoor dust chemistry and outdoor dust chemistry, I:O ratios can be calculated for each of the analytes for each particle size category. These ratios vary widely between buildings, analytes and particle sizes making it difficult to distinguish any trends or relationships. Therefore, the I:O ratios of all particles smaller than 250 μm were calculated for each building and analyte (Table 4.31 to Table 4.33). In each building, the majority of analytes generally show a decrease from outdoors to indoors, with the exception of organic content, which increases. Ca also shows an increase inside Buildings One and Two and is approximately equal inside Building Four.

Table 4.31: Indoor:outdoor ratios of street dust and indoor dust analytes for Building One

	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Jan	Feb	Mar	Apr
Al	0.4	0.41	0.56	0.56	0.47	0.58	0.61	0.51	0.63	0.42	0.64	0.63
Ca	1.08	1.11	1.5	1.48	1.15	1.05	1.14	1.27	1.45	1.45	1.29	1.4
Cu	0.47	0.53	0.48	0.51	0.53	0.46	0.51	0.65	0.63	0.46	0.43	0.6
Fe	0.41	0.45	0.47	0.63	0.62	0.61	0.6	0.63	0.49	0.48	0.45	0.58
K	0.47	0.61	0.4	0.45	0.46	0.67	0.44	0.4	0.52	0.43	0.53	0.6
Mg	0.67	0.51	0.41	0.54	0.46	0.6	0.44	0.58	0.43	0.58	0.47	0.66
Mn	0.49	0.67	0.68	0.44	0.45	0.47	0.47	0.41	0.65	0.42	0.69	0.41
Pb	0.43	0.58	0.44	0.67	0.61	0.6	0.47	0.4	0.47	0.62	0.69	0.58
Zn	0.47	0.62	0.66	0.6	0.56	0.4	0.6	0.43	0.69	0.63	0.56	0.45
Sulphate	0.89	0.72	0.87	0.77	0.95	0.72	0.77	0.91	0.86	0.92	0.73	0.87
Nitrate	0.44	0.51	0.54	0.62	0.57	0.7	0.4	0.54	0.57	0.44	0.57	0.44
Chloride	0.65	0.6	0.45	0.5	0.63	0.58	0.45	0.59	0.48	0.67	0.63	0.56
% Organics	1.08	1.26	1.26	1.35	1.1	1.36	1.33	1.12	1.5	1.23	1.12	1.35

Table 4.32: Indoor:outdoor ratios of street dust and indoor dust analytes for Building Two

	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Jan	Feb	Mar	Apr
Al	0.73	0.62	0.69	0.55	0.65	0.72	0.78	0.66	0.79	0.57	0.67	0.59
Ca	1.27	1.45	1.09	1.28	1.29	1.18	1.14	1.43	1.35	1.50	1.19	1.36
Cu	0.67	0.78	0.66	0.63	0.66	0.58	0.70	0.59	0.73	0.52	0.72	0.64
Fe	0.69	0.51	0.73	0.74	0.55	0.52	0.32	0.51	0.64	0.50	0.74	0.78
K	0.77	0.52	0.71	0.79	0.50	0.80	0.67	0.64	0.76	0.75	0.50	0.50
Mg	0.51	0.54	0.74	0.76	0.76	0.58	0.68	0.55	0.53	0.52	0.65	0.63
Mn	0.78	0.52	0.73	0.72	0.76	0.65	0.80	0.78	0.71	0.75	0.78	0.56
Pb	0.61	0.65	0.71	0.72	0.71	0.72	0.66	0.72	0.56	0.64	0.56	0.59
Zn	0.76	0.57	0.59	0.53	0.69	0.54	0.57	0.72	0.64	0.68	0.70	0.56
Sulphate	0.92	0.91	0.92	0.91	0.88	0.85	0.94	0.92	0.86	0.83	0.85	0.86
Nitrate	0.52	0.55	0.50	0.77	0.64	0.51	0.53	0.50	0.68	0.58	0.65	0.80
Chloride	0.76	0.64	0.80	0.78	0.61	0.64	0.72	0.68	0.52	0.75	0.51	0.63
% Organics	1.24	1.34	1.14	1.06	1.31	1.47	1.30	1.14	1.24	1.35	1.06	1.30

Table 4.33: Indoor:outdoor ratios of street dust and indoor dust analytes for Building Three

	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Jan	Feb	Mar	Apr
Al	0.96	0.90	0.92	0.98	0.92	0.87	0.90	0.99	0.91	0.96	0.87	1.00
Ca	0.78	0.90	0.89	0.77	0.78	0.82	0.87	0.83	0.86	0.86	0.81	0.79
Cu	0.82	0.86	0.72	0.77	0.82	0.87	0.82	0.79	0.94	0.83	0.74	0.80
Fe	0.92	0.88	0.80	0.96	1.00	0.89	0.90	0.92	0.91	0.87	0.94	0.87
K	0.90	1.02	0.96	0.89	0.87	0.93	0.91	0.99	0.88	0.93	0.87	0.95
Mg	0.99	0.89	0.85	0.97	0.92	0.87	0.92	0.88	0.90	0.89	0.88	0.89
Mn	0.91	0.92	0.87	0.97	0.91	0.92	0.98	0.95	0.90	0.87	0.94	0.93
Pb	0.86	0.93	0.89	0.89	0.85	0.99	0.94	0.89	0.88	0.85	0.89	0.95
Zn	0.77	0.80	0.78	0.71	0.77	0.80	0.81	0.77	0.80	0.72	0.76	0.78
Sulphate	0.83	0.92	0.90	0.91	0.87	0.86	0.92	0.80	0.92	0.92	0.87	0.82
Nitrate	1.41	1.52	1.39	1.22	1.57	1.75	1.73	1.47	1.67	1.53	1.87	1.41
Chloride	0.88	0.88	0.86	0.91	0.82	0.95	0.89	0.78	0.80	0.85	0.87	0.91
% Organics	0.74	0.74	0.70	0.73	0.83	0.76	0.75	2.69	2.48	3.11	2.12	1.15

Table 4.34: Indoor:outdoor ratios of street dust and indoor dust analytes for Building Four

	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Jan	Feb	Mar	Apr
Al	0.94	0.96	0.95	1.00	0.95	0.95	0.89	0.96	0.92	0.93	0.95	0.98
Ca	1.00	0.94	0.96	0.95	1.01	0.96	0.96	1.01	0.96	0.98	0.95	0.91
Cu	0.84	0.89	0.82	0.86	0.89	0.88	0.87	0.86	0.91	0.90	0.94	0.94
Fe	0.99	0.91	0.93	0.94	1.00	0.85	0.90	0.94	0.96	0.88	0.96	0.91
K	0.92	1.02	0.96	0.95	1.02	0.96	0.99	0.98	0.94	1.02	1.03	0.94
Mg	0.90	0.98	1.00	0.84	0.91	0.93	0.98	0.98	0.92	0.94	1.01	0.99
Mn	0.95	0.93	0.92	0.97	0.98	0.95	0.93	0.96	0.94	0.96	0.93	1.00
Pb	0.97	0.92	0.93	0.93	0.98	0.94	0.91	0.92	0.97	0.95	0.96	0.90
Zn	0.95	0.92	0.93	0.92	0.86	0.93	0.94	0.90	0.95	0.89	1.00	0.95
Sulphate	0.84	0.79	0.85	0.91	0.91	0.91	0.80	0.84	0.89	0.91	0.85	0.91
Nitrate	1.59	1.70	1.28	1.23	1.92	1.68	1.51	1.72	1.57	1.79	1.75	1.81
Chloride	0.85	0.86	0.93	0.87	0.79	0.86	0.86	0.79	0.77	0.81	0.86	0.76
% Organics	1.09	0.97	0.98	0.97	0.96	0.94	0.96	1.92	2.12	1.85	1.38	1.08

4.14.1.5 Variation with particle size

Determining analyte concentrations for different particle size ranges, has allowed any chemical variations between different particle sizes to be examined (Tables 4.35 to 4.41). Many of the analytes in dust collected outside from the roads show a similar relationship with particle size for all three roads. Al, K, Mn and chloride all increase in concentration for larger particle sizes for each road. Whereas, Cu, Zn and organic content all decrease with particle size. In all three roads sulphate concentrations decrease suddenly between 0-63 and 64-90 μm, then remain approximately equal. Different relationships with size are observed between the roads for Ca, Fe, Mg, and Pb with analyte concentrations for Road One often behaving differently to Roads Two and

Three. Particle size relationships inside the buildings are, generally, a reflection of the relationships observed outdoors for the appropriate road. The most notable difference is for Pb, which either shows an increase in concentration with increasing particle size or very little difference.

Table 4.35: Chemical content variation with particle size for Road One

	0-63 µm	64-90 µm	91-180 µm	180-250 µm
Al	302.8 (6.7)	393.0 (8.9)	508.1 (11.7)	664.1 (16.1)
Ca	246.9 (9.8)	323.1 (13.0)	418.4 (16.7)	543.5 (21.8)
Cu	18.7 (1.0)	12.8 (0.7)	9.0 (0.5)	6.4 (0.4)
Fe	359.8 (17.5)	335.4 (18.8)	293.3 (17.1)	264.7 (16.8)
K	97.2 (4.2)	126.1 (5.4)	164.2 (7.3)	212.3 (9.4)
Mg	58.8 (1.4)	53.5 (1.9)	47.6 (1.9)	42.9 (2.0)
Mn	22.2 (1.2)	28.9 (1.6)	37.8 (2.1)	49.2 (2.7)
Pb	20.9 (0.7)	18.6 (1.9)	16.4 (0.8)	15.2 (0.8)
Zn	33.8 (1.0)	23.6 (0.7)	16.9 (0.6)	11.7 (0.4)
Sulphate	381.9 (13.5)	75.3 (3.7)	75.0 (4.0)	76.7 (4.1)
Nitrate	11.7 (0.8)	11.8 (0.7)	11.7 (0.7)	11.7 (0.8)
Chloride	100.0 (9.5)	142.1 (13.8)	144.4 (14.3)	143.6 (14.6)
% Organics	35.1 (0.6)	13.8 (0.7)	14.1 (0.6)	13.7 (0.7)

$\mu g\ g^{-1}$ (Standard error shown in parenthesis)

Table 4.36: Chemical content variation with particle size for Road Two

	0-63 µm	64-90 µm	91-180 µm	180-250 µm
Al	439.3 (10.1)	682.6 (17.0)	1066.6 (28.5)	1647.7 (49.3)
Ca	519.8 (13.8)	368.1 (10.1)	256.5 (7.6)	178.7 (5.6)
Cu	12.7 (0.5)	7.3 (0.4)	4.2 (0.3)	2.4 (0.2)
Fe	237.7 (11.4)	254.8 (14.6)	265.7 (17.5)	284.4 (22.2)
K	130.3 (7.0)	185.5 (10.5)	258.3 (14.6)	360.1 (16.7)
Mg	50.6 (2.5)	49.0 (2.8)	50.7 (3.3)	50.8 (4.0)
Mn	33.4 (1.8)	46.2 (2.5)	63.7 (3.4)	89.5 (5.0)
Pb	26.2 (0.2)	23.6 (1.6)	23.1 (12.0)	22.1 (2.3)
Zn	22.2 (9.5)	10.7 (0.6)	4.3 (0.4)	2.0 (0.2)
Sulphate	40.2 (0.7)	7.8 (0.3)	7.6 (0.3)	7.7 (0.4)
Nitrate	10.6 (0.4)	10.2 (0.4)	10.1 (0.4)	10.1 (0.5)
Chloride	75.6 (9.4)	104.4 (12.8)	103.6 (12.3)	107.1 (13.2)
% Organics	25.9 (0.7)	9.9 (0.4)	9.6 (0.4)	9.7 (0.5)

µg g^{-1} (Standard error shown in parenthesis)

Table 4.37: Chemical content variation with particle size for Road Three

	0-63 µm	64-90 µm	91-180 µm	180-250 µm
Al	293.1 (9.9)	670.6 (15.4)	1025.2 (254)	1608.4 (39.6)
Ca	333.5 (15.9)	349.7 (21.4)	255.2 (29.6)	173.2 (38.8)
Cu	8.2 (0.2)	7.2 (0.2)	4.2 (0.1)	2.4 (0.1)
Fe	152.9 (9.5)	241.9 (13.6)	248.4 (15.4)	276.1 (17.4)
K	85.8 (4.6)	187.2 (6.8)	256.0 (10.0)	357.5 (14.2)
Mg	31.9 (1.42)	49.3 (1.5)	47.2 (1.8)	50.4 (2.3)
Mn	22.1 (1.2)	44.2 (1.7)	63.3 (2.4)	84.1 (3.5)
Pb	18.0 (0.6)	23.6 (0.9)	22.2 (1.1)	21.8 (1.6)
Zn	13.6 (0.7)	10.7 (0.6)	4.3 (0.6)	2.1 (0.7)
Sulphate	32.0 (0.4)	8.0 (0.3)	7.5 (0.3)	7.7 (0.4)
Nitrate	7.4 (0.4)	10.3 (0.3)	10.0 (0.5)	10.3 (0.5)
Chloride	47.9 (5.4)	111.4 (8.5)	102.6 (7.5)	105.8 (7.8)
% Organics	32.4 (0.5)	10.1 (0.7)	9.5 (0.7)	9.7 (0.8)

µg g^{-1} (Standard error shown in parenthesis)

Table 4.38: Chemical content variation with particle size for Building One

	0-63 µm	64-90 µm	91-180 µm	180-250 µm
Al	163.1 (8.8)	380.9 (9.0)	510.9 (17.7)	658.9 (16.2)
Ca	307.7 (20.1)	311.7 (17.9)	386.9 (25.7)	497.5 (29.3)
Cu	9.6 (0.7)	12.4 (0.8)	8.7 (0.7)	6.1 (0.4)
Fe	195.1 (21.6)	331.7 (31.2)	287.2 (21.8)	265.8 (28.7)
K	49.4 (3.2)	122.8 (6.3)	162.9 (8.1)	216.7 (11.1)
Mg	31.2 (1.6)	53.3 (2.4)	46.0 (2.2)	42.2 (2.3)
Mn	11.8 (0.9)	29.2 (1.9)	36.9 (1.9)	51.0 (3.6)
Pb	11.5 (0.5)	18.4 (1.0)	16.2 (0.9)	15.2 (0.7)
Zn	18.9 (1.5)	23.4 (1.2)	16.4 (1.0)	11.3 (0.7)
Sulphate	315.2 (12.4)	81.4 (6.0)	73.0 (5.4)	81.3 (6.9)
Nitrate	6.3 (0.8)	12.0 (1.6)	11.7 (1.3)	11.1 (1.2)
Chloride	57.8 (14.2)	133.1 (30.7)	145.2 (33.8)	136.5 (33.1)
% Organics	43.8 (1.6)	13.1 (0.4)	13.8 (0.5)	13.3 (0.7)

µg g^{-1} (Standard error shown in parenthesis)

Table 4.39: Chemical content variation with particle size for Building Two

	0-63 μm	64-90 μm	91-180 μm	180-250 μm
Al	203.8 (8.4)	393.9 (9.0)	496.9 (10.5)	639.5 (23.0)
Ca	309.3 (17.4)	313.6 (18.9)	396.1 (124.4)	524.2 (524.2)
Cu	12.0 (0.8)	12.4 (0.9)	8.5 (0.5)	6.2 (0.5)
Fe	220.9 (26.5)	323.3 (31.5)	288.5 (25.0)	258.5 (21.7)
K	65.1 (14.4)	124.9 (6.6)	163.5 (9.1)	213.4 (8.1)
Mg	36.7 (1.9)	53.9 (2.4)	48.9 (2.9)	43.7 (1.7)
Mn	16.2 (1.2)	29.5 (2.1)	38.8 (2.4)	48.8 (2.5)
Pb	14.2 (1.0)	18.0 (1.0)	16.5 (1.3)	15.4 (0.8)
Zn	21.3 (1.2)	22.0 (1.2)	16.5 (1.0)	11.1 (0.6)
Sulphate	338.5 (14.6)	77.1 (5.3)	73.9 (5.6)	77.0 (6.0)
Nitrate	7.1 (0.9)	12.3 (1.5)	11.8 (1.4)	11.2 (1.2)
Chloride	64.6 (15.2)	139.0 (33.1)	141.1 (34.8)	133.8 (30.5)
% Organics	43.3 (1.2)	13.3 (0.5)	13.6 (0.6)	13.7 (0.8)

μg g^{-1} (Standard error shown in parenthesis)

Table 4.40: Chemical content variation with particle size for Building Three

	0-63 µm	64-90 µm	91-180 µm	180-250 µm
Al	256.4 (10.9)	404.3 (21.4)	628.8 (44.8)	966.6 (79.1)
Ca	762.4 (15.2)	982.2 (11.3)	1288.8 (7.7)	1663.3 (5.2)
Cu	7.6 (0.5)	4.2 (0.6)	2.1 (0.3)	1.2 (0.2)
Fe	263.3 (11.1)	277.1 (17.2)	278.4 (16.4)	307.0 (24.6)
K	80.7 (6.4)	113.6 (13.6)	160.8 (20.5)	226.5 (23.5)
Mg	29.0 (1.6)	28.5 (2.7)	29.0 (2.6)	29.2 (3.0)
Mn	18.8 (1.8)	26.6 (2.4)	36.8 (4.5)	51.8 (4.6)
Pb	9.2 (1.2)	9.3 (1.5)	9.5 (1.5)	9.6 (2.5)
Zn	11.9 (0.6)	12.0 (0.8)	12.2 (0.4)	12.2 (0.1)
Sulphate	30.0 (0.6)	6.0 (0.3)	6.0 (0.4)	6.1 (0.4)
Nitrate	7.4 (0.6)	7.5 (0.7)	7.3 (0.4)	7.5 (0.6)
Chloride	52.9 (14.6)	73.4 (33.5)	73.3 (30.9)	74.8 (31.5)
% Organics	18.4 (1.4)	22.2 (0.4)	21.4 (0.4)	21.3 (0.3)
µg g^{-1} (Standard error shown in parenthesis)				

Table 4.41: Chemical content variation with particle size for Building Four

	0-63 µm	64-90 µm	91-180 µm	180-250 µm
Al	196.1 (9.6)	393.4 (25.6)	603.2 (28.4)	928.5 (62.0)
Ca	629.3 (13.8)	964.7 (27.8)	1294.8 (39.7)	1649.5 (53.9)
Cu	6.1 (0.2)	4.1 (0.2)	2.1 (0.1)	1.1 (0.1)
Fe	221.3 (14.2)	266.4 (18.6)	275.7 (28.5)	304.9 (25.1)
K	65.4 (6.0)	102.8 (9.5)	157.4 (15.3)	222.0 (23.0)
Mg	23.9 (1.6)	28.9 (2.0)	29.4 (2.0)	29.7 (2.9)
Mn	14.9 (1.2)	25.6 (1.9)	36.7 (2.5)	50.0 (4.0)
Pb	7.5 (0.7)	9.3 (1.1)	9.3 (1.1)	10.3 (1.6)
Zn	9.3 (0.4)	11.1 (0.6)	11.6 (0.5)	11.5 (0.5)
Sulphate	24.4 (0.7)	5.8 (0.2)	5.9 (0.2)	5.8 (0.2)
Nitrate	6.2 (0.5)	7.7 (0.7)	7.5 (0.6)	7.8 (0.7)
Chloride	41.1 (10.6)	74.4 (19.3)	71.3 (17.9)	70.1 (17.0)
% Organics	21.9 (0.9)	21.4 (1.0)	21.3 (0.9)	21.0 (1.0)
µg g^{-1} (Standard error shown in parenthesis)				

4.14.1.6 Correlations coefficients between elemental concentrations

Elemental analysis of dust smaller than 250 µm collected from the roads and buildings show several good relationships between the elemental concentrations (Tables 4.42 to 4.48). Interestingly, high correlations, which exist for inter-elemental concentrations in

dust, are also observed in airborne particle matter. Zn and Cu, Al and Ca, Al and Mn and Cu and Zn are all well correlated in street dust ($n = 288$, $p < 0.001$) and airborne particulate matter.

Table 4.42: Correlation matrix of elemental concentrations for Road One

	Al	Ca	Cu	Fe	K	Mg	Mn	Pb	Zn
Al	*	0.04	0.25	0.06	0.49	0.04	0.38	0.01	0.17
Ca		*	0.14	0.08	0.20	0.03	0.09	0.05	0.07
Cu			*	0.51	0.17	0.08	0.24	0.11	0.71
Fe				*	0.11	0.04	0.18	0.14	0.69
K					*	0.11	0.16	0.11	0.03
Mg						*	0.06	0.10	0.05
Mn							*	0.28	0.12
Pb								*	0.01
Zn									*
$n = 288$, $p < 0.05 = 0.195$, $p < 0.01 = 0.254$, $p < 0.001 = 0.321$									

Table 4.43: Correlation matrix of elemental concentrations for Road Two

	Al	Ca	Cu	Fe	K	Mg	Mn	Pb	Zn
Al	*	0.31	0.04	0.08	0.45	0.12	0.43	0.03	0.05
Ca		*	0.16	0.00	0.14	0.05	0.20	0.11	0.03
Cu			*	0.28	0.17	0.17	0.08	0.04	0.42
Fe				*	0.13	0.20	0.00	0.03	0.64
K					*	0.08	0.29	0.24	0.05
Mg						*	0.14	0.20	0.06
Mn							*	0.11	0.17
Pb								*	0.15
Zn									*
$n = 288$, $p < 0.05 = 0.195$, $p < 0.01 = 0.254$, $p < 0.001 = 0.321$									

Table 4.44: Correlation matrix of elemental concentrations for Road Three

	Al	Ca	Cu	Fe	K	Mg	Mn	Pb	Zn
Al	*	0.05	0.02	0.10	0.72	0.13	0.63	0.04	0.08
Ca		*	0.02	0.08	0.03	0.09	0.03	0.08	0.04
Cu			*	0.12	0.03	0.03	0.14	0.02	0.03
Fe				*	0.23	0.01	0.09	0.21	0.16
K					*	0.01	0.50	0.08	0.15
Mg						*	0.14	0.17	0.14
Mn							*	0.02	0.00
Pb								*	0.04
Zn									*
$n = 288, p < 0.05 = 0.195, p < 0.01 = 0.254, p < 0.001 = 0.321$									

Table 4.45: Correlation matrix of elemental concentrations for Building One

	Al	Ca	Cu	Fe	K	Mg	Mn	Pb	Zn
Al	*	0.32	0.09	0.05	0.03	0.02	0.11	0.03	0.06
Ca		*	0.05	0.05	0.07	0.48	0.01	0.05	0.55
Cu			*	0.78	0.27	0.13	0.57	0.10	0.46
Fe				*	0.48	0.14	0.47	0.38	0.58
K					*	0.05	0.58	0.10	0.24
Mg						*	0.30	0.26	0.52
Mn							*	0.29	0.00
Pb								*	0.18
Zn									*
$n = 288, p < 0.05 = 0.195, p < 0.01 = 0.254, p < 0.001 = 0.321$									

Table 4.46: Correlation matrix of elemental concentrations for Building Two

	Al	Ca	Cu	Fe	K	Mg	Mn	Pb	Zn
Al	*	0.38	0.69	0.68	0.37	0.49	0.42	0.01	0.38
Ca		*	0.45	0.22	0.39	0.05	0.71	0.50	0.47
Cu			*	0.55	0.40	0.80	0.53	0.47	0.52
Fe				*	0.12	0.72	0.02	0.08	0.73
K					*	0.20	0.47	0.03	0.03
Mg						*	0.08	0.07	0.58
Mn							*	0.60	0.11
Pb								*	0.07
Zn									*
$n = 288, p < 0.05 = 0.195, p < 0.01 = 0.254, p < 0.001 = 0.321$									

Table 4.47: Correlation matrix of elemental concentrations for Building Three

	Al	Ca	Cu	Fe	K	Mg	Mn	Pb	Zn
Al	*	0.09	0.70	0.38	0.47	0.30	0.12	0.27	0.26
Ca		*	0.13	0.57	0.00	0.55	0.45	0.23	0.27
Cu			*	0.06	0.28	0.51	0.02	0.09	0.58
Fe				*	0.07	0.06	0.00	0.72	0.13
K					*	0.12	0.09	0.04	0.18
Mg						*	0.79	0.12	0.05
Mn							*	0.16	0.01
Pb								*	0.01
Zn									*
$n = 288, p < 0.05 = 0.195, p < 0.01 = 0.254, p < 0.001 = 0.321$									

Table 4.48: Correlation matrix of elemental concentrations for Building Four

	Al	Ca	Cu	Fe	K	Mg	Mn	Pb	Zn
Al	*	0.19	0.31	0.00	0.64	0.25	0.78	0.07	0.28
Ca		*	0.07	0.51	0.14	0.18	0.21	0.39	0.21
Cu			*	0.26	0.01	0.03	0.01	0.25	0.00
Fe				*	0.01	0.34	0.05	0.40	0.17
K					*	0.34	0.78	0.04	0.66
Mg						*	0.31	0.58	0.22
Mn							*	-0.32	0.36
Pb								*	0.08
Zn									*
$n = 288, p < 0.05 = 0.195, p < 0.01 = 0.254, p < 0.001 = 0.321$									

4.14.2 Street dust magnetic properties

A summary of the magnetic measurement results from the street dust samples is presented in Table 4.49. Once this information was obtained it was possible to make a correlation between the various magnetic measurements and LOI. A summary of the correlation coefficients obtained is given in Table 4.50.

It is interesting to note that a much wider range of LOI was measured amongst the 210 samples analysed in this study, than in previous work (*i.e.* Xie *et al.*, 2000). However, there is still a similar, strong correlation between $\chi_{FD\%}$ and LOI in this study and the work of Xie *et al.*, (2000). This is illustrated in Figure 4.54, which indicates a R^2 value of 0.79 ($n = 210$, $p < 0.001$, f ratio = 209.35) compared to the value of 0.61 reported by Xie *et al.*, (2000). Equally good correlation coefficients were observed when the data were calculated for the three seperate roads (Figure 4.55).

Similar relationships were discovered between street dust LOI and other magnetic parameters (Table 4.50). For instance, the χ_{ARM} parameter is also shown to be significantly correlated with LOI (Figure 4.56). Furthermore, when the data are separated into different sample populations (Figure 4.57), there is evidence to suggest that the samples from Road One possess different magnetic properties to those of Roads Two and Three.

Table 4.49: Mineral magnetic results of street dusts (n = 210)

Magnetic Parameter	Units	Mean	Standard Error
χ_{LF}	$x10^{-7}$ m^3 kg^{-1}	58.83	5.81
χ_{HF}	$x10^{-7}$ m^3 kg^{-1}	55.45	5.47
$\chi_{FD\%}$	%	4.37	0.28
SOFT	%	17.59	0.22
HARD	%	4.27	0.41
S-ratio	none	-0.76	0.01
χ_{ARM} /SIRM	$x10^{-5}$ Am^{-1}	0.51	0.01

Table 4.50: Correlation coefficients between LOI and mineral magnetic characteristics

Magnetic Parameter	χ_{LF}	χ_{HF}	$\chi_{FD\%}$	SOFT %	HARD %	S-ratio	χ_{ARM} /SIRM
Correlation coefficient	0.47	0.44	0.79	0.08	0.50	0.15	0.71
$n = 210, p < 0.05 = 0.195, p < 0.01 = 0.254, p < 0.001 = 0.321$							

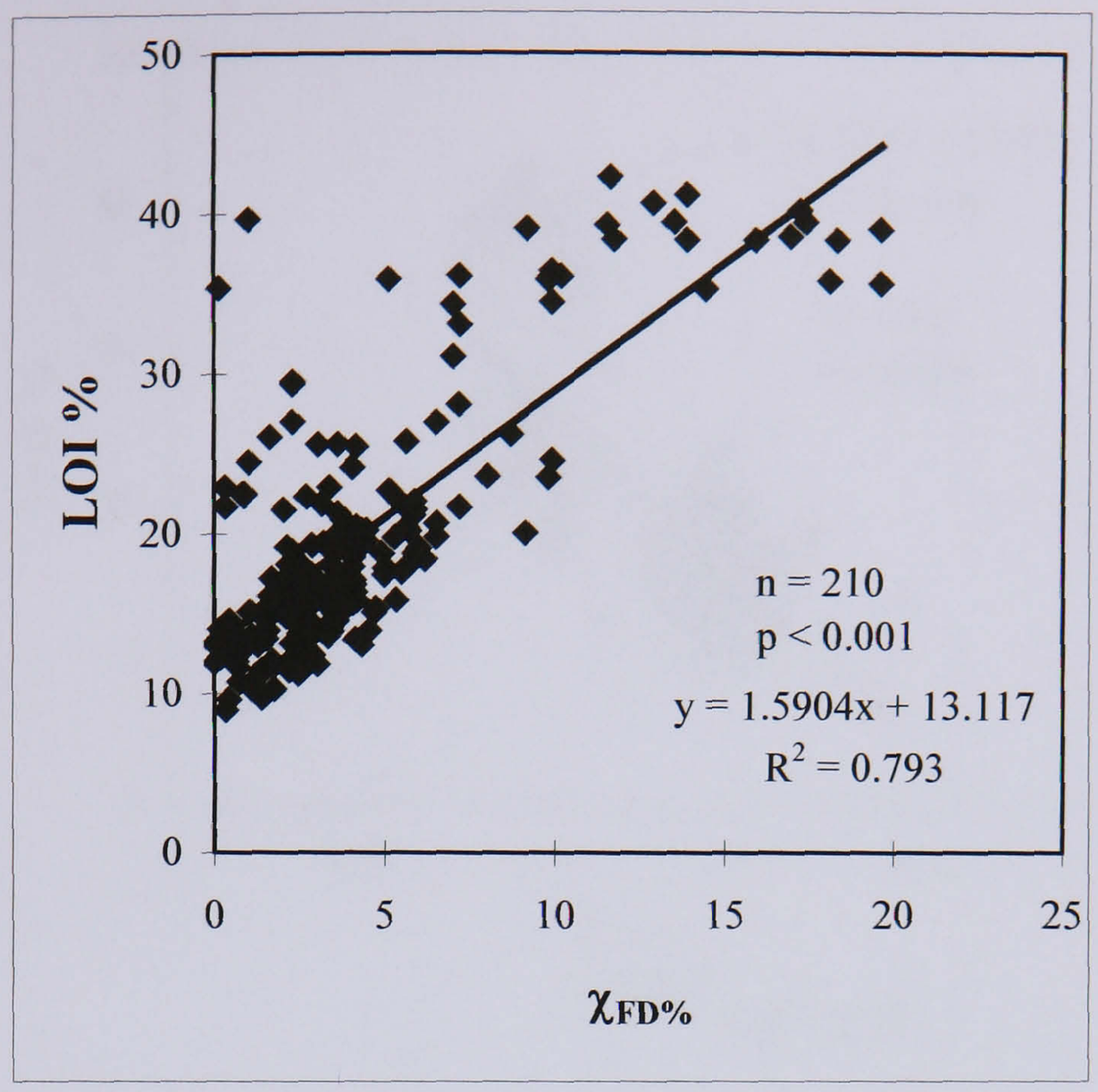


Figure 4.54: The relationship between χFD% and LOI in urban street dust

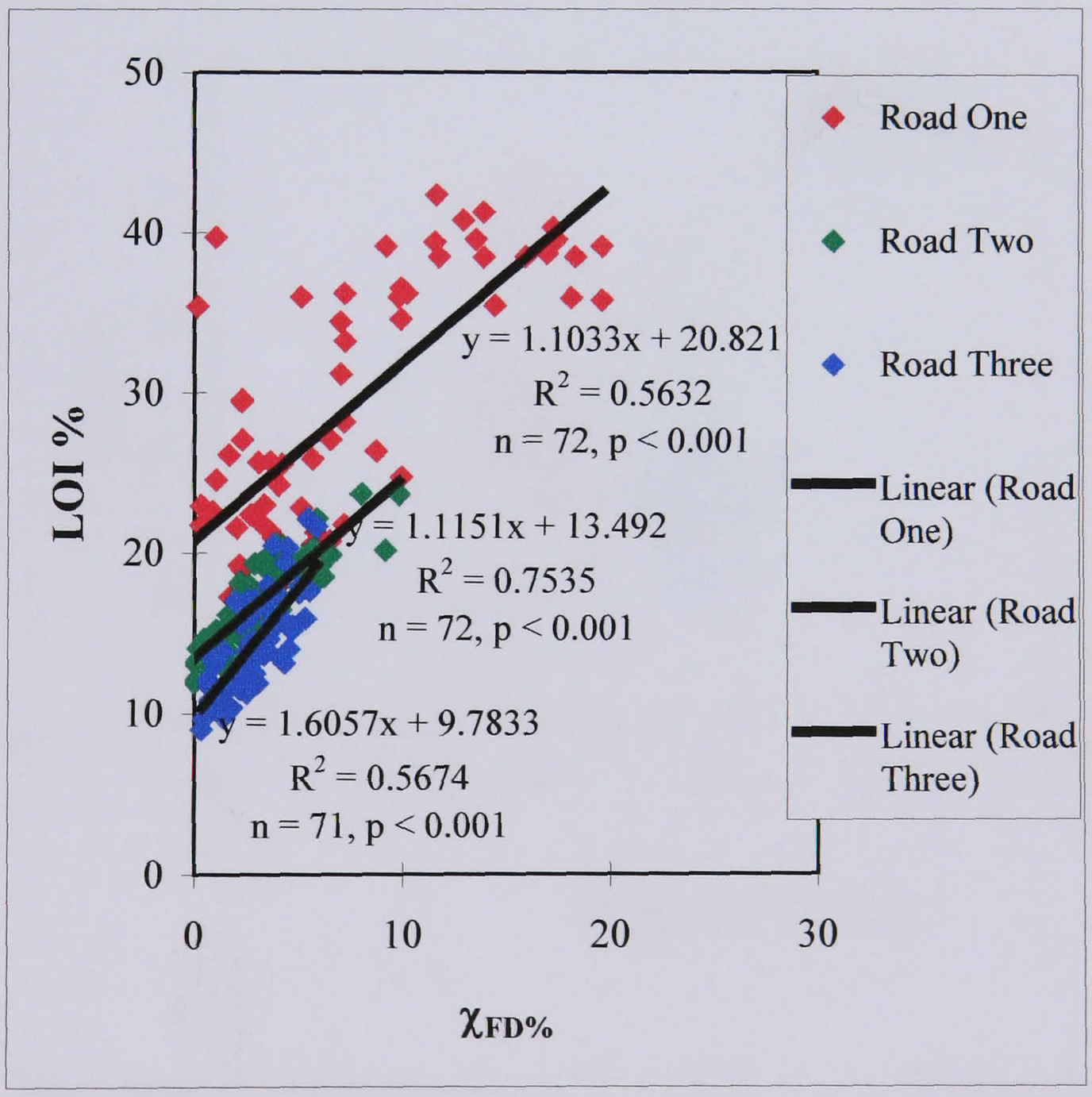


Figure 4.55: The relationship between χFD% and LOI in urban dust at three sites

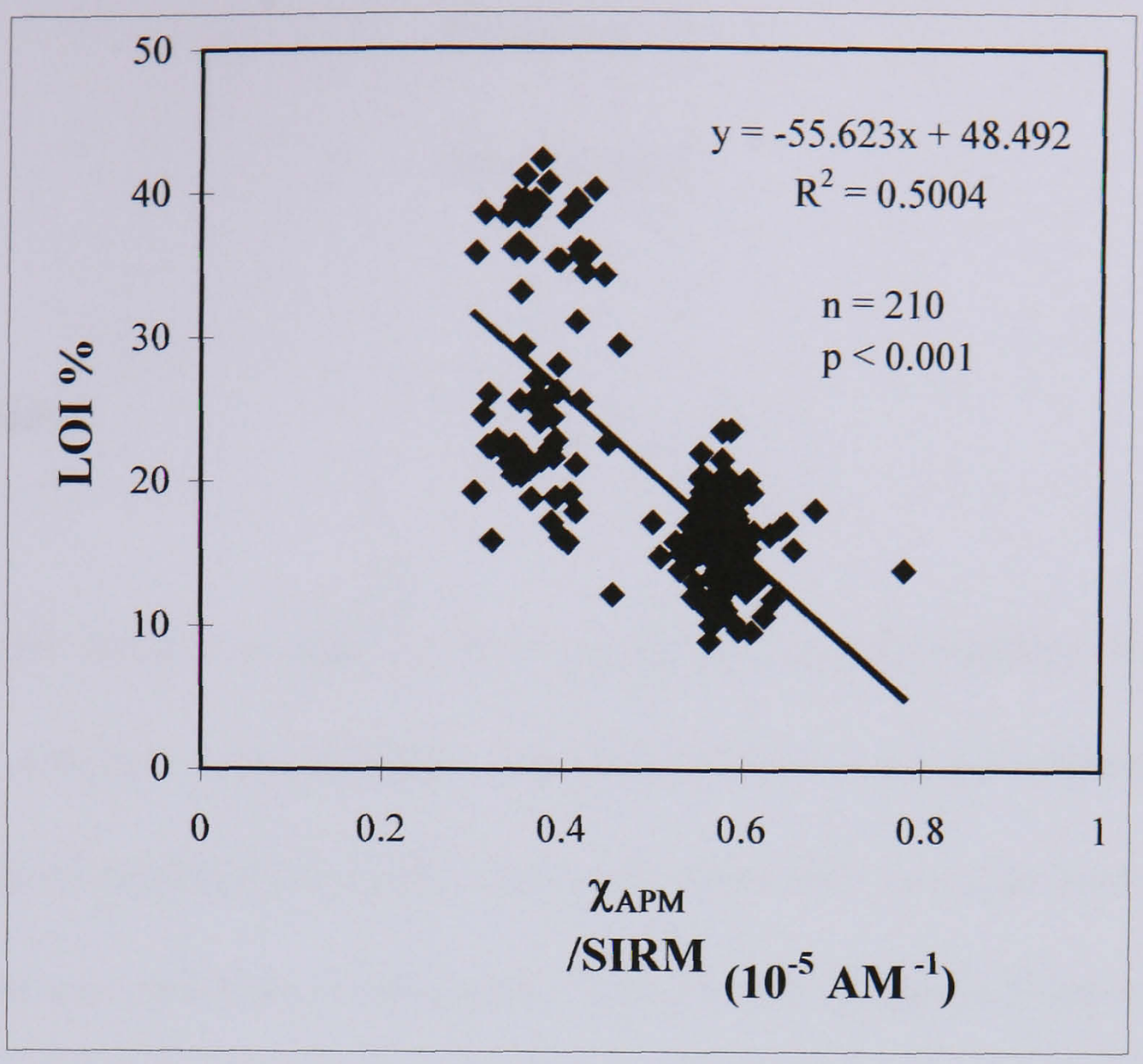


Figure 4.56: The relationship between χARM/SIRM and LOI in urban dust

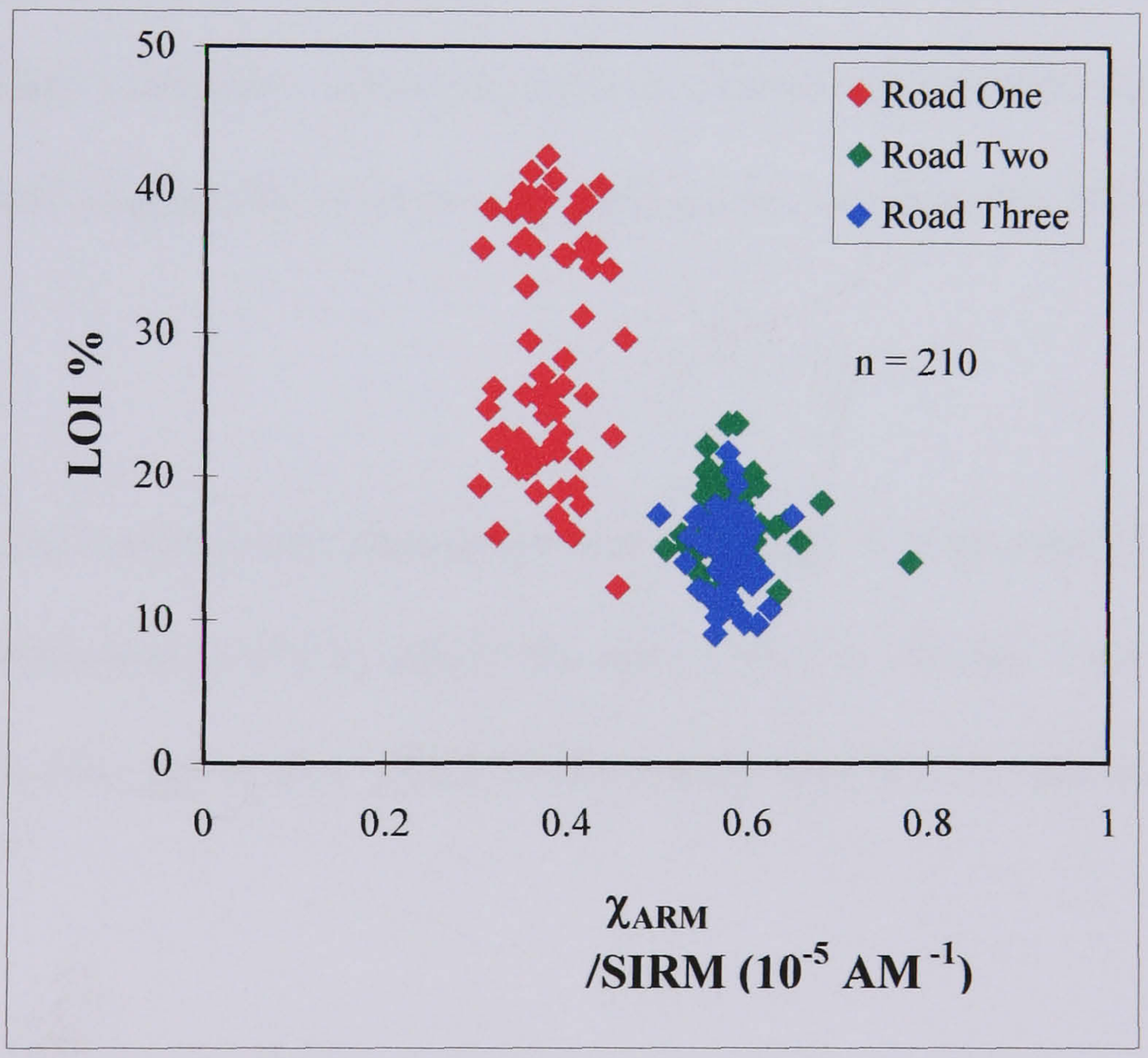


Figure 4.57: The relationship between χARM/SIRM and LOI in urban street dust at three sites

Chapter 5

Discussion

5.1 Introduction

The experimental studies conducted have assessed the relationships between indoor concentrations, outdoor concentrations and personal exposure of respirable particulate matter. Analysis of settled dust, indoor dust and street dust has also been carried out in order to identify any possible relationships between the different phases of particulate. Overall, the results show that indoor concentrations are related to outdoor concentrations, although the relationship is being affected by other variables, likely to be local meteorology. In addition, chemical analysis of street dust, settled dust and airborne particulate matter suggest the existence of relationships between the different phases of dust.

By discussing the results under appropriate sub headings, it is intended to expand upon the observed relationships and to satisfy the aims stated in Chapter Two. In addition to the sections, covering the results, a final section integrates the different experiments.

5.2 Relationships between indoor and outdoor airborne particulate matter and seasonality

Over the monitoring period of one year, a significant relationship was observed between indoor and outdoor respirable particulate concentrations (Section 4.2) ($R^2 = 0.551$, $n = 143$, $p < 0.005$), with peaks in outdoor concentrations often reflected indoors (Figure 4.1 and 4.2). These results agree with those reported by Monn and Becker (1999) and also Geller *et al.,* (2002), who recorded R^2 values of 0.55 and 0.53, respectively. A mean indoor:outdoor ratio of 0.42 (SE = 0.02) is similar to indoor:outdoor ratios recorded during other studies (Li, 1994) and suggests a loss of particulate during penetration indoors. However, despite the relatively low SE measured for the indoor:outdoor ratio, it has been observed that the indoor:outdoor ratios can alter from one day to the next, even when building conditions remain the same. It seems likely that other factors are affecting the quantity of particulate matter penetrating indoors.

When indoor:outdoor relationships are broken down into individual seasons, there are clear differences between summer/spring and autumn/winter (Table 4.1). This suggests that local meteorology is having a pronounced effect upon indoor air quality. During summer and spring, outdoor particulate concentrations are significantly greater than during autumn and winter. It is possible that this is due to the drier conditions of the summer, enabling the greater re-suspension of street dusts and soil, combined with a lower quantity of particulate matter removed from the atmosphere, through the washout effect. Indoor concentrations are also lower during autumn and winter, although indoor

concentrations are likely to be simply mirroring outdoor concentrations. The greatest indoor:outdoor ratios occur during summer with building use a likely explanation. For example, building occupants may be opening windows for ventilation and greatly increasing the air exchange rate between outdoor and indoor air.

5.3 Relationships between airborne particulate matter of different diameters

For indoor samples in Buildings One, Two and Three and outdoor samples at Roads One and Two, the concentrations of TSP, PM_{10}, respirable particulates and $PM_{2.5}$ are all closely related and follow almost identical trends with time (Section 4.3). Namdeo *et al.,* (1999) also observed a close relationship between TSP, PM_{10} and $PM_{2.5}$ in an urban street canyon in Nottingham, UK. Inside Buildings One and Two the difference in mean particulate concentration between all the four size categories is very small, with $PM_{2.5}$ accounting for 91% of TSP inside Building One and 80% of TSP inside Building Two (Figure 4.7 and 4.8). Inside Building Three, the difference is greater and $PM_{2.5}$ accounts for 73% of TSP (Figure 4.9). These results show that the majority of airborne particulate matter inside the buildings is within the $PM_{2.5}$ size category. This would be expected, as the building shell, through entrapment, may be removing larger particles. In addition, larger particles that penetrate into the building will deposit quickly under the relatively still indoor conditions, meaning a faster decay rate when compared to smaller particles. Fogh *et al.,* (1997) found that 4 μm particles decayed at over twice the rate of 2 μm particles. For outdoor samples, the majority of TSP is still accounted for by $PM_{2.5}$, with $PM_{2.5}$ accounting for 69% and 59% of TSP at Roads One and Two, respectively (Figure

4.10 and 4.11). These values are greater than those measured by Namdeo *et al.,* (1999) who reported that $PM_{2.5}$ accounted for between 20% of TSP during the day and 80% of TSP during the night time. The percentage of PM_{10} to TSP has also been studied around the world: 54 – 55% in Mexico (Cicero-Fernandez *et al.,* 1993), 57% in Geneva (Monn *et al.,* 1995) and 50% for the US national average (Lipfert, 1994). The lower indoor percentages support the suggestion that the building shell filters larger particles more effectively than smaller particles during air movement indoors. In addition, the deposition of larger particles will be far less important outdoors due to the much higher amount of air turbulence.

The breakdown in particle size can be used to give an indication of the sources of particulate matter present in each location. Between the roads, $PM_{2.5}$ accounts for a greater percentage of TSP at Road One than at Road Two. This suggests that the dominant source of particulate matter at Road One generates predominantly fine particles, likely to be the diesel buses regularly using the road. At Road Two, the percentage of $PM_{2.5}$ accounting for TSP is noticeably lower. Although road traffic still appears to be the dominant source of particulate matter at Road One, other sources may be becoming more dominant, such as building weathering and soil re-suspension, which produce relatively coarse particles when compared to vehicle emissions. The effect of these outdoor results on the indoor results is further evidence that outdoor particulates penetrating indoors is the dominant source of particles in all three buildings. However, it is interesting to note that even though Buildings One and Two are both located opposite one another at Road One, the difference in the particle size breakdown is clear, with a

greater percentage of $PM_{2.5}$, accounting for TSP inside Building One. This suggests that the shell of Building One is more efficient at removing particles than Building Two. A likely reason for this is the double door system present at Building One, whilst Building Two has a poorly fitting single door system, which easily allows particles of any size to penetrate. It is worth noting that the flow of people through the doors of the two buildings is approximately equal, so this is unlikely to be responsible for any measured difference between the buildings.

5.4 Simultaneous measurements of particulate concentrations inside Buildings one, two and three

Clear differences have been observed between the mean respirable particulate concentrations recorded simultaneously inside the foyers of Buildings One, Two and Three (Figure 4.12). Building Three foyer contains the lowest mean particulate concentration at 10.1 $\mu g\ m^{-3}$ (n = 37, SE = 0.6). Concentrations measured inside Building One are approximately twice as high at 20.4 $\mu g\ m^{-3}$ (n = 37, SE = 1.4), whilst concentrations recorded inside Building Two are over three times greater at 32.2 $\mu g\ m^{-3}$ (n = 37, SE = 2.2). If it is being assumed that outdoor particles are the main source of indoor particles for these buildings, these results can be used to give information on both the source strength of particles outside the buildings and also the efficiency by which particles are penetrating indoors.

Source strength of particles outside Building Three appears to be considerably weaker than outside Buildings One and Two, and is demonstrated by the relatively low respirable particulate concentrations measured inside this building. However, it should also be noted that the foyer of Building Three is generally more 'open', with the corridors running off the foyer having no doors. The foyers in Buildings One and Two are not like this and have corridors with doors that are closed when not in use. It can be assumed that most of the particulate present in the foyer of Building Three is transgressing through the main door and also being re-suspended from the floor and other surfaces in the foyer. Therefore, it is possible that the lower concentrations measured in Building Three are partly due to a dilution effect caused by particulates escaping from the foyer into other parts of the building, but mainly due to the weaker source strength outside. When comparing Buildings One and Two the source strength outside the buildings can be considered as being equal. However, Building Two contains a significantly greater concentration of particulate matter. Therefore, these results suggest that particles are penetrating more efficiently into the Building Two foyer than into the foyer of Building One. This is further evidence that the double door system of Building One offers greater protection from ambient particulate penetrating indoors than the single door system at Building Two.

5.5 The relationships between meteorology and indoor and outdoor particulate concentrations

Meteorological conditions can affect both the concentrations of particulate matter outdoors and also the quantity of particulate matter penetrating indoors. Recording meteorological conditions simultaneously with indoor and outdoor particulate measurements for Building One has enabled an assessment of the affect meteorology has upon indoor and outdoor particulate concentrations (Section 4.5). From previous literature, it can be seen that wind direction, wind speed, atmospheric pressure, precipitation and relative humidity can all effect indoor:outdoor particulate relationships (Chan, 2002).

One of the most significant meteorological factors observed affecting particulate concentrations indoors and outdoors is wind direction (Section 4.5.1). Both indoor and outdoor particulate concentrations at Road One and inside Building One are significantly related to the direction of wind (Figure 4.14 and 4.15). In addition, the indoor:outdoor ratio is also significantly related to the direction of the wind. Other studies into indoor:outdoor ratios of particulate matter have observed no significant relationship between indoor:outdoor ratio and wind direction (Morawska *et al.,* 2001). The reason this building shows a relationship is likely to be because it is located in a street canyon. Outdoor particulate concentrations are significantly greater during perpendicular wind conditions and decrease rapidly when the wind is flowing parallel to the road. Winds perpendicular to the canyon may be producing vortexes that are trapped

within the canyon, causing particulate concentrations to build up to high concentrations. During parallel wind conditions polluted air is effectively replaced by ambient air (considered to be less polluted in this situation), so that particulate concentrations do not build to high concentrations. The greatest indoor:outdoor ratios are observed during perpendicular wind conditions. There are two possible explanations for this. Firstly, rotating vortexes formed inside the canyon by the perpendicular wind may be producing pressure gradients between indoors and outdoors, causing outdoor air to be drawn indoors. Secondly, wind flowing parallel to the canyon is likely to move through the canyon at a higher velocity. Therefore, a Bernoulli effect may be operating to ensure that air pressure inside the canyon is lower hence air from outside is not being drawn indoors.

For the whole year, indoor concentrations and indoor:outdoor ratio show no discernable relationship to wind speed (Section 4.5.2). However, outdoor concentrations show a significant negative correlation (Figure 4.21) (R^2 = -0.35, n = 119, $p < 0.001$). This is expected, as a greater wind speed would cause a cleaning effect inside the canyon due to more efficient mixing between canyon air and cleaner ambient air (Huang *et al.,* 2000). When the results are broken down into seasons (Table 4.2), outdoor concentrations only show a significant negative relationship to wind speed during the winter (R^2 = -0.54, n = 30, $p < 0.001$), whilst indoor concentrations show a significant negative correlation to wind speed during summer (R^2 = -0.41, n = 35, $p < 0.001$). Indoor:outdoor ratio is positively correlated to wind speed during the summer (R^2 = 0.33, n = 27, $p < 0.01$). A plausible reason for the seasonal variation in correlation coefficient observed for

outdoor particulate concentrations may be that during the winter an increase in wind speed does not lead to any re-suspension of settled dust due to the damp ground conditions typical of December, January and February. Hien *et al.,* (2002) also observed a decrease in the re-suspension of surface soil following rainfall. Because of this, a cleaning effect is observed as canyon air is effectively replaced by cleaner ambient air. However, during the drier months an increase in wind speed leads to re-suspension of settled dust raising the concentration of particulates in ambient air. Therefore, this counteracts any cleaning effect caused by the replacement of canyon air with ambient air. A positive relationship between indoor:outdoor ratio and wind speed during the summer is likely to be a combination of wind speed and building use. For example, windows may be opened during the summer by building occupants, meaning that a relatively small increase in wind speed will greatly increase the penetration of ambient air indoors.

Significant positive correlations exist between indoor ($R^2 = 0.26$, $n = 130$, $p < 0.01$) and outdoor ($R^2 = 0.5$, $n = 119$, $p < 0.001$) particulate concentrations and atmospheric pressure for the year as a whole (Section 4.5.3). When the results are broken down into seasons (Table 4.3), significant correlations for outdoor particulate concentrations exist for all seasons except autumn. For indoor particulate concentrations, significant correlations exist for summer and autumn. It is unlikely that variations in pressure alone directly effects particulate concentrations, as no obvious mechanism for this appears to exist. It is more likely that variations in atmospheric pressure are indicative of other meteorological conditions, such as temperature inversions. The highly variable seasonal

correlations for indoor:outdoor ratio and atmospheric pressure are not what would be expected; as it was thought high atmospheric pressure would induce outdoor air to be drawn into the building. This does not appear to be occurring, therefore, in Building One it may be assumed that varying atmospheric pressure is largely out-weighed by other meteorological factors and building use conditions (such as people movement, ventilation and heating systems).

As expected, precipitation significantly effects particulate concentrations indoors and outdoors with the greatest particulate concentrations occurring during days with zero precipitation (Section 4.5.4). A study by Hien *et al.,* (2002) also found that periods of high precipitation, in the form of rainfall, significantly decreased daily particulate concentrations. Rainfall duration and rainfall quantity both effect particulate concentrations in a similar way, although rainfall quantity seems to have a greater influence than duration. In addition, rainfall intensity has no significant effect upon either indoor or outdoor particulate concentrations. These results seem to suggest that the length of time a precipitation event lasts has no bearing on the quantity of particulate matter removed from the atmosphere and it is the quantity of precipitation falling, regardless of time scale, which is the controlling factor. For example, if the same quantity of precipitation fell during one hour or three hours, then approximately equal amounts of particulate would be removed from the atmosphere. It is often assumed that following a precipitation event particles washed out of the atmosphere can quickly become re-suspended, so that particulate levels rapidly return back to previous concentrations (Jennings, 1998). These results would suggest the opposite, because if

this was the case extended periods of light rainfall would have a greater influence on particulate concentrations than short heavy rainfall, even though the quantity of rainfall may be the same. The reason why this may not be occurring is because of the relatively damp climate of the UK. For example, days with precipitation often occur during high humidity conditions, so that when a precipitation event is over the ground remains damp for long periods of time following the event. Therefore, the particles washed out of the atmosphere are unlikely to be re-suspended back into the atmosphere for a considerable period of time.

5.6 Relationships between PM_{10} and particle count

The variation of both particle count and PM_{10} indoors is smaller and generally more gradual than outdoor measurements, which is a trend also observed by Kopenon *et al.*, (2001) and Chan (2002). The most noticeable difference in particle count is that Building Two contains significantly higher counts than either Building One or Three (Table 4.4). This is further evidence of the poor protection the building shell of Building Two offers against outdoor air pollution when compared to Building One. In addition, there is very little difference between the particle count measured outdoors and inside Building Two, with an indoor:outdoor ratio of 0.92. In contrast, the indoor:outdoor ratio of particle count for Building One is 0.66. This shows that although the particles being counted are all sub-micron in diameter, the building shell still offers some protection against them penetrating into the building. The simultaneous PM_{10} measurements also shows this difference, but to a lesser degree. For example, the indoor:outdoor ratio of

PM_{10} for Building One and Two was 0.58 and 0.70, respectively, suggesting that the larger particles are indeed removed more efficiently than the sub-micron particles detected by the particle counter. Particle count at Road One is almost three times greater than at Road Two, clearly indicating the effect of the diesel buses that travel along Road One. The effect of the buses on Road One is also shown by the measurements taken inside the buildings, with Buildings One and Two containing a significantly greater number of sub-micron particles than Building Three ($n = 42$, $p < 0.001$). In all three buildings and at both roads there were significant correlations between particle count and PM_{10} (Table 4.5) ($n = 42$, $p < 0.001$). It seems from other studies that, whether a significant relationship exists between PM_{10} and particle count is site specific as some studies report, a significant relationship exists (Monn, 2001), whilst others do not (Keywood *et al.,* 1999). A significant correlation suggests that sub-micron particles and gravimetric PM_{10} are originating from the same sources, which is likely to be the diesel buses at Road One and in the case of Road Two general background vehicle emissions. These correlations also suggest that sub-micron particles are contributing some mass to gravimetric PM_{10}; however, the correlations are not strong, suggesting that such a contribution is minimal.

PM_{10} and particle count both follow almost identical trends with time at both roads and inside all three buildings (Figure 4.27 to 4.31). However, when the diurnal variation of PM_{10} and particle count is examined closely, there appears to be a small lag between when particle count begins to increase and when PM_{10} begins to increase. Similarly, PM_{10} also begins to decrease prior to particle count. The presence of this lag may be due

to the sub-micron particles counted by the particle counter remaining resident in the atmosphere for a longer period of time than larger particles, which contribute most to gravimetric PM_{10}. Sub-micron particles measured by the particle counter will remain resident in the atmosphere and not settle due to their low mass, therefore, particle count concentrations will remain elevated until polluted air is replaced with clean air.

At every indoor and outdoor location night time particle count and PM_{10} concentrations are lower than daytime levels, which suggests some form of traffic input to particulate levels and probably the occurrence of re-suspension indoors by the movement of building occupants. However, between each location there are notable differences in the daily variation of particle count and PM_{10}. Inside Buildings One and Two there are distinct morning and afternoon peaks in both PM_{10} and particle count, highlighting the contribution of traffic sources to airborne particulates inside these buildings. In Building Three, however, no peak in either PM_{10} or particle count occurs during the morning or afternoon, suggesting that traffic sources are less important inside this building. Particle count and PM_{10} show morning and afternoon peaks at Road One, but only particle count shows any morning and afternoon peak at Road Two. The lack of morning and afternoon peaks for PM_{10} at Road One suggests that particle count is a better indication of traffic sources than PM_{10}. The results measured during this research agree with Harrison *et al.,* (1999) who conclude that particle count is a better indication of traffic emissions as PM_{10} are influenced more strongly by non-traffic sources.

5.7 Scanning electron microscopy of indoor and outdoor airborne particulate matter

A visual comparison of scanning electron micrographs taken of indoor and outdoor airborne particulate samples illustrates the differences and similarities between the particulates collected at each location (Section 4.7). The most noticeable difference is observed in the quantity and size of collected particles (Plate 4.1 and 4.2). The average size of particles collected from outdoor samples appears to be generally much larger than indoor samples. The amount of coverage on the filter paper for outdoor samples is also many times greater than for indoor samples. Both of these differences would be expected, as gravimetrically, outdoor samples are normally between 50 to 100% greater than the corresponding indoor samples. Most of the particles inside Building One and outdoors at Road One are composed of accumulations of very small particles (1 to 10 nm), forming chains and spherulites. What is unclear is whether the particles are agglomerating as they deposit onto the filter paper or whether they are agglomerating in the atmosphere before collection. It seems likely that it will be a combination of the two factors. However, particles of this type almost certainly originate from combustion sources and have also been identified as originating from diesel engine emissions (Berube *et al.,* 1999). In addition, the presence of spherical, porous particles of approximately 1 μm in diameter also suggests particles being present from combustion sources. Particles of this type have been identified as originating from various combustion sources in other studies (Zou and Hooper, 1997; Rose and Long, 1996). These spherical particles have been observed in both outdoor and indoor samples.

Because the majority of particles collected indoors are sub-micron in diameter and the majority of outdoor particles are significantly larger, this suggests that larger particles are being effectively filtered by the building shell and/or depositing out of the atmosphere rapidly upon entering the building. However, the presence of a large quantity of particles smaller than 1 μm show that smaller particles can easily penetrate through the building shell.

5.8 Chemical analysis of indoor and outdoor airborne particulate matter

Particulate chemistry can give an indication of the sources from which the particles are originating. Particles inside Building One and outside at Road One were analysed for the elements Al, Ca, Cu, Fe, K, Mg, Mn, Pb and Zn and the anions chloride, nitrate and sulphate.

5.8.1 Elemental analysis

Elements can be roughly classified as being either urban or natural and in this research the categories suggested by de Miguel *et al.,* (1997) were used. Urban elements are considered as Cu, Mg, Pb and Zn and natural elements as Al and Mn. A third group of elements can be considered as being from a mixed origin and include Ca, Fe and K. For each of the elements analysed indoor concentrations are lower than outdoor concentrations, suggesting the source of all analysed elements is outdoors (Table 4.6 to 4.9). However, the amount of reduction between outdoors to indoors varies significantly

between the elements showing a variation between the ability of the elements to penetrate through the building shell. Interestingly, the natural elements (Fe, Al, Ca, K and Mn) have low indoor:outdoor ratios of less than 0.30. Whereas, the urban elements Cu, Mg, Pb and Zn have the greatest indoor:outdoor ratios (ranging from 0.46 for Mg to 0.57 for Zn), suggesting that they penetrate indoors most effectively. A probable source of these urban elements is exhaust emissions from the buses using Road One. It has been suggested that Zn in combination with Br and Sb could be used as a potential marker element for motor vehicle emissions, due to engine oil containing high concentrations of the element (Huang *et al.,* 1994). However, zinc can also be emitted in large quantities by oil powered power plants and oil refineries. As there are no oil powered power plants or oil refineries in the region, it seems likely that the majority of zinc present inside and outside of this building originates from traffic emissions. In addition, there is evidence that Cu can be traced back to motor vehicle emissions (de Miguel *et al.,* 1997). The results obtained during this research agree with these findings.

The conclusions drawn from the indoor:outdoor measurements are also supported in the correlation coefficients between indoor and outdoor concentrations (Table 4.6 to 4.8). The only significant correlations are observed for Cu, Pb and Zn, again suggesting that the presence of these elements is mainly derived from outside. As well as indoor:outdoor ratios, indoor:outdoor correlation coefficients can also give an indication of particle size and likely sources. The correlation coefficients suggest that Cu, Mg, Pb and Zn are associated with the finest particles. However, Al, Ca, Fe, K and Mn seem to be associated with larger particles and do not penetrate indoors as efficiently. The most

likely source of these latter elements is soil re-suspension in the case of Al (Ferguson and Kim, 1991) and Ca (Spengler and Thurston, 1983; De Miguel *et al.,* 1997), meaning the majority of particles originating from this source would be relatively coarse. Fe and K can originate from various sources, with the low indoor:outdoor ratio, suggesting mainly a natural source. However, Fe can also be found in vehicle emissions (Matzca and Maher, 1999), but it is likely that the contribution of Fe from this source may be sufficiently low so as not to have any significant effect upon the results.

Correlation coefficients can also be used to determine the likelihood of elements originating from the same source. Significant correlations between elements exist both indoors and outdoors. In outdoor samples significant correlations ($p < 0.01$) are observed between several elements including Al-Ca, Al-Cu, Al-Mn, Ca-Cu, Ca-Mg, Ca-Mn, Ca-Zn and Cu-Zn. However, the only significant correlation to exist in indoor samples is between Cu and Zn. Interestingly, these are also the two elements with the highest indoor:outdoor ratios. Ca is significantly correlated to many of the elements, reflecting its wide range of sources, such as wind blown soil, organic material, building weathering and its presence in many building materials. If Ca is removed from the correlations the only remaining significant relationships exist between Al-Cu, Al-Mn and Cu-Zn. Both Cu and Zn are grouped into the urban elements category and are significantly related to each other both indoors and outdoors, suggesting they originate from the same source, which can be considered further evidence of these elements originating from vehicle related emissions. Both Al and Mn are categorised as natural elements and are significantly related to one another outdoors, but not indoors. The

insignificant relationship indoors and the low indoor:outdoor ratio suggests these elements are associated with larger particles so do not penetrate indoors efficiently. Also, because these elements are significantly associated with each other a possible source of both elements is soil re-suspension. In addition, Al is also significantly related to Cu outdoors, a possible explanation for this finding is that Al may also be originating from traffic sources, with wind blown soil the major source. This is possible as many vehicles contain Al in engine components or as part of the car body. Therefore, degradation of these vehicles may cause a small amount of particulate Al to be produced.

There appears to be no seasonal variation of concentration outdoors for most of the elements (Table 4.10 and 4.11). Only Ca (greatest during summer) and Mn (greatest during spring/summer) show any discernible seasonal difference, with all the other elements either being variable from month to month or remaining relatively stable. This is also reflected indoors with only Ca and Al, both greatest during spring and summer, showing any noticeable variation. Therefore, it appears that for most elements the sources remain at a similar strength throughout the year. This is not the case for Ca, however, as a distinct seasonal variation is observed. The summer increase in Ca is most likely to be associated with an increase in soil re-suspension during the drier spring and summer months as Ca is often a major component of suspended soil (Spengler and Thurston, 1983; De Miguel *et al.*, 1997).

5.8.2 Anion analysis

Regression analysis between indoor and outdoor anion concentrations are distinctly different for each anion (Section 4.8.2). Sulphate (R^2 = 0.65) and nitrate (R^2 = 0.44) have an indoor:outdoor coefficient significantly greater than chloride (R^2 = 0.23). These results suggest that sulphate and nitrate are associated with smaller particles and chloride with coarser particles, therefore, penetrating indoors less efficiently. This suggestion is also supported by the indoor:outdoor ratios for each anion. Sulphate (0.64) and nitrate (0.51) have the greatest indoor:outdoor ratios, while chloride (0.21) is noticeably lower (Table 4.2). The ratio for sulphate agrees well with findings of other studies that have measured indoor:outdoor ratios of sulphate between 0.8 and 0.9 (Li and Harrison, 1990; Lee *et al.*, 1997). It is also generally agreed that sulphate is predominantly associated with finer particles and is not found in airborne particles greater than approximately 2.5 μm in diameter (Clayton *et al.*, 1992; Jones, *et al.*, 2000).

The concentrations of all three anions show a notable variation with season (Table 4.13 and 4.14), with the same seasonal variation observed indoor and outdoors. However, the seasonal differences are not as pronounced indoors as they are outdoors. The sharp increase of chloride during the winter is almost certainly due to rock salt being applied to nearby roads as a de-icing agent. Willison *et al.*, 1989 suggests that rock salt application to roads can be an important source of airborne particulate chloride. Sulphate and nitrate are both greater during summer, with this seasonal variation also observed by other researchers (Kasper and Puxbaum, 1998; Paoletti *et al.*, 2002). The

increase in particulate nitrate and sulphate during summer is likely to be caused by the photo-chemical oxidation reactions of NO_2 and SO_2 being increased by a higher quantity of UV light during the summer months (QUARG, 1996).

5.8.3 Chemical analysis of size fractionated airborne particulate matter

Between locations there is no significant variation in the chemical composition of airborne particulate matter and the relationships between particle size and chemistry are very similar (Section 4.8.3). Chloride and nitrate show no variation with particle size and sulphate generally shows an increase in concentration as particle size decreases (Table 4.15). These findings agree well with results published by other researchers, for example, Clarke *et al.,* (1999) found the same particle size relationships for chloride, nitrate and sulphate. There are two factors that are likely to be responsible for the higher proportion of sulphate present in finer particles. Firstly, the formation of sulphate by photo-chemical oxidation of SO_2 produces fine particles (Willison *et al.,* 1989). Secondly, primary vehicle emissions of sulphate particles, especially by heavy duty diesel engines, will generally emit particles in the fine fraction.

5.9 Personal exposure

A significant relationship exists between personal exposure measurements and both indoor and outdoor concentrations (Section 4.9). A strong correlation would be expected between personal exposure and indoor concentrations as the individual used for personal

exposure measurements spent the majority of their day indoors and only went outside for an average of 35 minutes per day. The majority of research into personal exposure has also observed strong correlations with indoor concentrations (Koistinen *et al.*, 2001). A good correlation is also observed between personal exposure and outdoor measurements (Figure 4.33), but as expected, is not as significant as the relationship between personal exposure and indoor measurements. Significant correlations between outdoor concentrations and personal exposure measurements have also been reported (Lioy *et al.*, 1990). The results measured here suggest that outdoor particulate concentrations are the likely driving force behind indoor concentrations and, therefore, personal exposure inside this building. For this particular location this means that the majority of particulate, to which building occupants are exposed, is originating from diesel emissions. This is an important finding due to the possible health implications associated with diesel particulate.

The regression analysis of personal exposure and both indoor and outdoor measurements show that the Y intercept (personal exposure) is approximately 7 $\mu g\ m^{-3}$. Other studies have found intercepts indoors ranging from between 2 to 42 $\mu g\ m^{-3}$ and outdoors between 4 to 63 $\mu g\ m^{-3}$ (Lioy *et al.*, 1990; Koistinen *et al.*, 2001; Ogzkaynak *et al.*, 1996). This indicates that even if outdoor and indoor concentrations were zero, there would still be a measurement of 7 $\mu g\ m^{3}$ for personal exposure. This result supports the theory of a 'personal cloud' of particulate matter existing around an individual and, from these results, may add as much as 7 $\mu g\ m^{-3}$ to the exposure level measured for an

individual. It has also been suggested that the quantity of personal cloud is directly related to the amount of activity of the individual (Adgate *et al.,* 2002).

A height profile measurement of respirable particulate matter also shows that the greatest concentrations exist at approximately 2 m above ground (Figure 4.32), the approximate adult breathing height. This finding agrees well with Micallef *et al.,* (1998), who also observed the greatest indoor concentrations of airborne particulate matter at approximately 2 m above ground level, demonstrating that people breathing at difference heights are exposed to different levels of airborne particulate matter. The reason as to why particulate concentration is greatest in this zone may be due to several factors, such as the mass and density of respirable particulate matter. It is also likely that human activity is largely responsible for the increase of particulate matter at this height above ground, a view shared by Micallef *et al.,* (1998).

5.10 Particulate variation within a street canyon

Respirable particulate concentrations recorded on opposite sides of the same road at roof level and kerbside level have shown, as would be expected for such closely co-located monitors, significant correlations between the four sets of measurements (Table 4.16). However, from the results it is clear that wind direction is a very important factor in determining the concentration of particulate matter at specific sites within the street canyon.

Rooftop measurements are almost always lower than corresponding kerbside locations (Table 4.17), obviously due to the kerbside measurements being close to the source of particulate matter. The majority of research into height profiles of particulate matter inside street canyons has found an exponential decrease of concentration with height (Zoumakis, 1995) and that the decay rate for particulate matter is generally greater than for gaseous pollutants (Reiter *et al.,* 1979; Rohbock *et al.,* 1980).

The vertical differences measured at Road One are most noticeable during perpendicular wind direction, likely to be due to vortices forming within the canyon. During perpendicular wind directions, leeward concentrations are significantly greater than concentrations recorded on the windward side. This can be explained by a perpendicular wind causing a simple vortex to form inside the canyon. These vortices have been observed forming during many studies into pollutant dispersion and air movement within street canyons (Huang *et al.,* 2000; Buckland, 1996; Berkowicz *et al.,* 1996). Within the vortex, relatively clean rooftop air is drawn down the windward side of the canyon and then moves across the road in the opposite direction to the wind at roof level, bringing particulate matter from the road across to the leeward side of the canyon. This effect causes pollutant concentrations on the leeward side to be greater than the windward side (Croxford and Penn, 1998).

Under certain conditions, a small vortex can form at the base of the windward building and cause pollutants to accumulate to higher concentrations (Huang *et al.,* 2000). However, this effect was not observed in this canyon. During parallel wind directions, it

was observed that particulate concentrations at the same height on opposite sides of the canyon are approximately equal. This is probably due to polluted air being more efficiently replaced by cleaner ambient air.

5.11 Dust soiling rates and settled dust analysis

5.11.1 Dust soiling rates

It is not possible to directly relate the dust soiling rates published in other papers with the values measured here, due to the wide range of methods used. However, other researchers have obtained comparable results using different methods of between 22 and 37 mg m^{-2} d^{-1} (Rufus *et al.,* 1998). For the month of April, in Building Three there is a high peak in the dust soiling rate (Figure 4.37). Although there was a small amount of construction work being carried out in the vicinity of this building, it is unlikely that this was the cause of the peak. A possible explanation is contamination of the slides during the exposure period leading to an artificial increase in the mass of dust collected. However, no obvious contamination mechanism was observed during the study. Dust soiling rates for the three buildings show no noticeable seasonal variation, with soiling rates for Building Three being fairly constant after the removal of the anomalous result for April. The soiling rates for Buildings One and Two are more variable, but also follow no obvious seasonal trend.

Bate and Coppin (1990) have suggested a threshold limit of 200 mg m^{-2} day^{-1} for dust soiling to be considered a nuisance, while other literature propose threshold limits varying from 133 to 650 mg m^{-2} d^{-1} (Vallack and Shillito, 1998). When compared to these suggested thresholds, the soiling rates measured in these buildings can be considered as relatively low (Figure 4.38). Results show that the foyer in Building Two has a higher average dust soiling rate than the other two buildings ($p < 0.05$, $n = 12$). After removal of the anomalous results for April, this difference is still statistically significant ($p < 0.05$, $n = 11$). A likely explanation for the elevated dust soiling rates in Building Two is due to the main door of this building being almost in constant use and also being poorly fitted, leaving visible gaps around the door when closed. This allows outside air to easily penetrate the building shell. When the building is not in use, particulate matter can then continue to settle on surfaces inside the building. In contrast, the double door system at Building One offers a more efficient barrier to ambient particulates, reducing the rate of dust soiling inside the foyer. A paired t-test comparing the dust soiling rates inside Building One to the dust soiling rate inside Building Three, indicates no significant difference between the two sets of data, further suggesting the effectiveness of the double door system of Building One filtering out ambient particles generated by vehicles within the street canyon.

Although soiling rates are consistently greater in Building Two than in Building One, the soiling rates inside Buildings One and Two are well correlated with a similar trend over time (Figure 4.39). This may indicate that the dust settling inside these two buildings is from similar sources, probably re-suspended road dust and diesel exhaust

particulate. A regression analysis of the dust soiling rates inside Building One against dust soiling rates inside Building Two further illustrates this relationship giving an R^2 of 0.57 ($p < 0.02$, $n = 12$).

5.11.2 Particle chemistry

The influence of traffic related particulate matter on the indoor settled dust is clearly shown by the chemical analysis of individual particles (Figure 4.40 to 4.42). The most distinct seasonal variation in settled dust chemistry is observed for Na-Cl rich particles. During the winter Na-Cl rich particles accounted for approximately 50 – 60 % of all particles by number in each building. This decreases rapidly throughout spring to a summer background level of just 5 – 10 %. These particles are likely to be originating from re-suspended rock salt applied to roads as a de-icing agent (Willison *et al.,* 1989). The results also show that Na-Cl rich settled dust particles are present in equal amounts for all particle sizes, suggesting that re-suspended road dust can contribute a range of particle sizes to airborne particulate matter. In a study of airborne particles Clarke *et al.*, (1999) also found no significant relationship between chloride and particle size. It is of note that marine contributions to the presence of sodium and chlorine rich particles in these buildings are likely to be lower than in other UK cities as Wolverhampton is located approximately 125 km away from the nearest coastline.

Si-Fe rich particles also show a seasonal variation (Figure 4.40 to 4.42), although not to the extent of Na-Cl rich particles. Inside all three buildings the percentage of Si-Fe rich

particles is greater during the summer, rising from 10 – 20 % to approximately 40 % of all particles. This seasonal pattern, however, is more pronounced inside Buildings One and Two than inside Building Three. Si can be categorized alongside Fe as an element of mixed origin is often considered to have originated from soil, re-suspended road dust or building materials (Wang *et al.*, 1996). It seems probable that the Si-Fe rich particles are originating from both of these sources as soil re-suspension and street dust re-suspension by wind and traffic will all increase during the drier summer months. In Buildings One and Two, road dust re-suspension may be the dominant source due to the high volumes of traffic using Road One. At Building Three soil re-suspension and street dust re-suspension by wind is likely to be the dominant source as Road Two does not carry high traffic levels.

5.11.3 Particle morphology

Settled dust particle size shows a seasonal variation, with the average particle size being larger during the summer months than the winter months (Figure 4.49). Rufus *et al.*, (1998) in a study of deposited dusts in houses, also found that larger particles were deposited during the summer. A t-test between winter samples and summer samples shows that the summer/winter difference is statistically significant for all three buildings ($p < 0.05$, $n = 12$). These larger particles may originate from wind blown soil or street dust, which were not re-suspended during the damper winter period. In Buildings One and Two, for every sample the particle size is smaller than for the corresponding Building Three samples. This is probably to be due to the presence of smaller diesel

exhaust particles present in samples from Buildings One and Two, which are not present at Building Three.

The aspect ratio of the settled dust shows no discernible seasonal trend in any of the three buildings and the ratio is highly variable from month to month (Figure 4.52). However, the aspect ratio for settled dust inside Buildings One and Two is lower than Building Three in every sample. Visual examination of the electron micro-graphs of particles collected inside these two buildings show the presence of sub-micron, spherical particles. Particles of this type tend to be produced by combustion processes, with the only form of combustion in the local vicinity being the traffic on Road One. Occasional agglomerations of very small particles, only several nanometres in diameter, were also observed inside Buildings One and Two. Diesel particles often occur in this form (Berube, *et al.,* 1999), therefore this may indicate the presence of diesel particle contamination. Both the small spherical particles and the agglomerations were absent in the samples from Building Three. Regression analysis between the aspect ratio of particles inside Building One with the aspect ratio of particles inside Building Two shows a very strong correlation between the two samples, giving an R^2 value of 0.819 (Figure 4.53) ($p < 0.001$, $n = 12$). This may also indicate that the particles inside the two buildings originate from the same sources, therefore, agreeing with the conclusion drawn from the dust soiling rate measurements.

5.11.4 Chemical deposition rate

As well as being an important loss mechanism for airborne particles in general, deposition flux can also be measured for individual chemical species. Deposition flux for heavy metals and other chemical species have not been widely measured over recent years, with studies mainly focussing on Pb. Deposition rates measured by Al-radady (1991) are approximately three times greater than deposition rates recorded during this research. However, his measurements were taken in relatively old houses containing leaded paint and windows with lead trimmings. It seems likely that these fittings would have added to the concentration of several metals in these houses, therefore, the results are understandable.

Elemental deposition rates recorded inside Building One do not appear to be related to the chemical composition of airborne particulate matter. Interestingly, those elements that are present in the greatest quantity in airborne respirable particulate matter have the lowest deposition rate. The elements with the greatest deposition rates (Fe, Al, Ca, K) are classified as originating from mixed or natural sources, whilst it is the elements from the urban sources group (Cu, Mg, Pb and Zn) that have the lowest deposition rates (Tables 4.19 to 4.21). In terms of the elemental concentration of airborne particulate matter, it is the urban elements that have the greatest concentrations and the natural/mixed source elements with the lowest concentrations. This observation suggests that factors other than the chemical composition of airborne particulate matter are influencing the deposition of elements. It may be expected that the elements with the

greatest concentrations in air would also be deposited at the greatest rate, but this does not appear to be the case. It is generally accepted, that particle size is a very important factor in determining the deposition rate of airborne particulate matter (Leg and Price, 1980; Heynie, 1986; Kim *et al.,* 2000). Although the deposition rate of particulate matter is dependent on many factors, in terms of chemical deposition rates, larger particles add a far greater mass than smaller particles. Other experiments have suggested that the urban elements are associated with the smallest particles and the natural/mixed elements associated with the larger particles. From this, it can be concluded that the natural/mixed elements will be deposited at a greater rate, as elements associated with smaller particles will remain airborne for a longer period of time. For all three buildings it is the natural/mixed elements that have the greatest elemental deposition rates, although there were significant differences between the deposition rates between the buildings, which may reflect the relative sources of particulate. Inside Building Three, Ca deposition was far greater than Buildings One and Two. However, there was very little difference between elemental deposition rates between Buildings One and Two. The urban elements Cu, Zn and Pb were all greater in Building One and Two. This would be expected if Cu, Zn and Pb could be traced back to vehicle emissions.

Anion deposition rates inside Building One follow the same trend as the chemical composition of airborne respirable particulate matter, with sulphate having the greatest rate and nitrate and chloride demonstrating far smaller deposition rates. However, sulphate is, generally, associated with very small particles. A likely reason for sulphate having a very high deposition rate in comparison to the other anions is likely to be due

to sulphate being in concentrations several orders of magnitude greater in airborne particulate collected inside this building. Therefore, even though sulphate is generally associated with fine particles, it still deposits in high quantities. The deposition rate of sulphate inside Building Three is many times lower than those recorded inside Buildings One and Two. This gives an indication of the source of sulphate, with Buildings One and Two seeming to have a very strong localised source, likely to be the buses using Road One.

Significant variations between winter and summer deposition rates are observed inside all three buildings (Table 4.19 to 4.21). Al, Ca and Pb deposition rates are all greatest during the summer, whilst K, Mg and Zn are all greatest during the winter. This seasonal variation was observed in all three buildings. Altering rates of re-suspension, due to meteorological differences between summer and winter, is a possible explanation for these seasonal differences. For example, if the source of the urban elements Mg and Zn is traffic emissions, then in the damper winter, these elements will be more efficiently washed out of the atmosphere prior to them entering the buildings, therefore, decreasing the deposition rate during winter. A likely source of Al and Ca is soil re-suspension, so that in summer when a greater quantity of soil is re-suspended their deposition rate will increase. Deposition rates for Pb are also greater during the summer. It is possible that Pb is also originating from re-suspended soil due to historical Pb contamination caused by leaded petrol. Nitrate and chloride both show a significant winter to summer variation, however, sulphate remains approximately equal throughout the year. Chloride deposition in winter is approximately 5 to 10 times greater than

during summer. Again, this is likely to be related to the application of rock salt to roads as a de-icing agent, which is then suspended by the movement of traffic or brought indoors on peoples' shoes and then suspended by cleaning and the movement of building occupants. Nitrate deposition increases between 50 and 100% in the summer compared to the winter in all three buildings, probably due to the secondary formation of nitrate particles in the atmosphere by photochemical oxidation reactions of NO_2 (Kasper and Puxbaum, 1998; Paoletti *et al.,* 2002).

5.12 Street dust and indoor dust analysis

5.12.1 Seasonal variation

Only chloride shows any discernible seasonal variation with all of the other analytes and elements either varying very little or altering erratically from month to month (Section 4.14.9). Chloride increases by approximately 250 to 400% at all three roads and inside all four buildings. This increase is almost certainly caused by applying rock salt to roads as a de-icing agent.

5.12.2 Variation between Roads

The greatest variation for all of the elements is observed for Ca, with dust from Road Three containing almost 400 % more Ca than either Road One or Two (Tables 4.22 to 4.24). This observation suggests that the majority of dust present in Road Three is

originating from Ca rich soil. As this is a residential area it is likely to be washed onto the road from domestic gardens and grass embankments, which line long stretches of the road. Out of all the analytes, sulphate shows the greatest variation and is an order of magnitude greater at Road One than either Road Two or Three. Again, this suggests that diesel buses are a very strong local source at Road One. In addition, elements that may also be associated with vehicle emissions, Zn and Cu, are also present in concentrations twice as high at Road One than at Roads Two and Three.

5.12.3 Variation between buildings

The variation in dust chemistry inside the buildings closely follows the variation outdoors in that traffic related analytes (Cu, Zn and Sulphate) are all significantly greater inside Buildings One and Two (Table 4.25 to 4.28). In addition, the concentrations of analytes inside Buildings One and Two are almost identical and follow a very similar trend over time; however, concentrations inside Building Two are slightly greater than Building One. The slight increase in concentration indoors can be attributed to two factors. Firstly, more street dust may be being walked into the building as the entrance to Building One incorporates a porch with a plastic abrasive 'shoe-cleaning' floor; no such porch exists inside Building Two. Secondly, particulate penetration into Building Two is considered to be more efficient than into Building One. Therefore, once these airborne particles settle, they will contribute to indoor dust.

5.12.4 Indoor and outdoor relationships

Organic content is the only constituent that continually shows an increase in all three buildings from outdoors to indoors (Table 4.31 to 4.34), this was also observed by Fergusson and Schroeder (1985). Ca increases from outdoors to indoors in Buildings One and Two, whilst all other analytes show a decrease in concentration. These results agree with other studies into street dust, which also show many chemical constituents decreasing in concentration from outdoors to indoors, except when an internal source is present (Rasmussen *et al.,* 2001). The increase of Ca indoors suggests an indoor source of the element, most likely to be the degradation of interior building materials, such as plaster. The decrease in concentration of almost all the other elements at all the locations suggests that the sources of these elements is outdoors and is becoming mixed with dust originating from indoors, which may contain a large variety of other elements or organic materials not detected in the analysis. The increase of organic material from outdoors to indoors suggests that this is in part responsible for the decrease in analyte concentrations, due to a 'dilution' effect. This organic material is most likely to be composed of shedded skin and degraded hair and to contain a very large variety of chemical constituents, many of which would not be detected by the analytical procedure performed on the dusts.

Nitrate concentrations are greater in Buildings Three and Four than outside on the appropriate street, suggesting that there is an indoor source of nitrate. A potential source of indoor nitrate is through the reaction of ammonia (present in many household

cleaners) with nitric acid (formed from NO_2). An unknown fraction of the nitrate is likely to be in the form of ammonium nitrate. Suh *et al.,* (1994) concluded that it may be this reaction causing indoor airborne nitrate concentrations to be greater than corresponding outdoor samples in a study of domestic homes in Pennsylvania. The reason why this is only seen in Buildings Three and Four may be due to the different cleaning regimes of these buildings. As Building Four is a domestic house, it is likely that more ammonia based cleaning products, such as bleach, are used in this building than in the University buildings. The floor in Building Three has imitation marble effect and is polished on a daily basis, therefore, it is unlikely that the cleaning chemicals used on this floor contain ammonia due to the damage they can cause to this type of floor surface. In addition, the floors in Buildings One and Two are composed of plastic/rubber anti-slip material which are cleaned with vacuum cleaners and very rarely wet cleaned, therefore, the presence of ammonia is likely to be relatively low.

5.12.5 Variation with particle size

In general, analyte concentrations show the same relationships with particle size between each of the roads (Tables 4.35 to 4.41). Al, K, Mn and chloride all increase with particle size, suggesting that their source is likely to be from processes such as the re-suspension of surface soil or the degradation of building material. Al, K and Mn are all classified as either natural or mixed origin elements, therefore, supporting this suggestion. Interestingly, Cu and Zn, which are both elements categorised as originating from urban sources, decrease in concentration with increasing particle size. This

suggests that they are associated with sources producing fine particles, likely to be vehicle emissions, therefore agreeing with earlier conclusions. Ca, Fe, Mg and Pb concentrations at Road One show different relationships with particle size than at the other two roads. This shows that much of the street dust at Road One is originating from different sources likely to be traffic emissions, tyre wear and vehicle degradation.

The increase in chloride concentration with increasing particle size is difficult to explain, as there are no continual chloride sources in the local vicinity. A possible explanation is remnant chloride remaining after road salting during the winter, as this will mainly be in the form of large particles or aggregate that becomes broken down over time.

Sulphate shows a distinct variation with particle size, decreasing rapidly after the 63 μm size category. This is seen at all three roads (Tables 4.35 to 4.37). It is generally accepted, that sulphate is associated with very fine particles in airborne particulate matter (Monn and Sachaeppi, 1993; Clayton *et al.*, 1992; Jones, *et al.*, 2000). It can be assumed that the sulphate present in street dust originates from settled airborne particles, with the results observed here supporting this assumption. Although sulphate concentration decreases rapidly with increasing particle size, the concentration still remains relatively high in the largest size category. Therefore, it seems likely that fine sulphate particles are remaining physically bound to larger particles and being analysed as part of the larger size fraction.

Analyte relationships with particle size inside the building are generally a reflection of relationships outside (Tables 4.38 to 4.41), again suggesting that the source of indoor dust is almost entirely dust brought in from outside. The only noticeable difference is that Pb increases with particle size for indoor samples. When a building contains leaded paint, this relationship is often seen due to the degradation of the paintwork. However, no leaded paint remains in any of the four buildings as it has either been removed or painted over. The only other possible sources of indoor Pb is the degradation of fixtures and fittings inside the buildings or the suspension of historic dusts. However, it seems unlikely that this would be sufficient to increase the concentration of Pb indoors as much as is observed in the samples.

5.12.6 Correlations coefficients between elemental concentrations

Significant associations exist between elemental concentrations at all roads and inside all buildings (Tables 4.42 to 4.48). The associations observed in airborne particulate matter are also seen to exist in street and indoor dust. Associations also exist in street and indoor dust that are not present in airborne particulate matter. This may be due to street dust and indoor dust having a greater number of sources than respirable airborne particulate matter, therefore, more associations are likely to exist. Other studies into indoor dust and street dust have also found significant associations between many different elements (Rasmussen *et al.,* 2001). Zn is significantly correlated with Cu in each Building, except Building Four, and each road, except Road Three. This is further evidence that Cu and Zn can both be traced back to vehicle emissions as very few cars

use Road Three. The natural elements, Al and Mn, are also significantly associated with each other at all locations except Building One and Building Three. Although associations exist between elements in dust that do not exist in airborne particulate matter, the presence of associations that exist in both suggest that there is some relationship between these two phases of dust, although it is difficult to determine any quantitative relationship using chemistry alone.

5.13 Street dust magnetics

Low frequency magnetic susceptibility (χ_{LF}) represents the total contribution of ferrimagnetic minerals, while high frequency magnetic susceptibility (χ_{HF}) represents the total contribution of paramagnetic and canted antiferromagnetic minerals (Dearing, 1999). Frequency-dependent susceptibility percentage ($\chi_{FD\%}$) detects the proportion of ferrimagnetic minerals of superparamagnetic (SP) domain size (Dearing *et al.*, 1996a). SOFT percentage is approximately proportional to the concentration of the ferrimagnetic minerals (e.g. magnetite (Fe_3O_4) and haematite (γFe_2O_3)) within a sample, while HARD percentage is approximately proportional to the concentration of the canted antiferromagnetic minerals (e.g. haematite (αFe_2O_3) and goethite ($\alpha FeOOH$)) within a sample (Oldfield & Richardson, 1990). The S-ratio is a reverse field measurement that discriminates between ferrimagnetic and canted antiferromagnetic mineral types (Robinson, 1986), while χ_{ARM}/SIRM indicates the domain size of ferrimagnetic minerals.

The mean χ_{LF} and χ_{HF} values (58.83 and 55.45 x10^{-7} m^{-3} kg^{-1}, respectively) of the samples when compared to published values for other environmental materials (Dearing, 1999), indicate that the street dusts contain a moderately high concentration of magnetic minerals similar to those of some igneous rocks, coarse metamorphic rocks and some top soils and burned soils. The magnitude of these values mean that, if present, the signatures of diamagnetic and paramagnetic minerals are dominated by the signatures of canted antiferromagnetic and/or ferrimagnetic minerals and, therefore, indicates that their contributions to the total susceptibility are not significant. Soft percentage and hard percentage values (mean 17.59% and 4.27%, respectively) indicate that the content of ferrimagnetic 'magnetite-type' minerals (low coercivity) are more dominant than canted antiferromagnetic 'haematite-type' minerals (high coercivity). This is further supported by the S-ratio, which shows a mean value of –0.76, which is indicative of a dominance of magnetically soft minerals. However, some S-ratio values (~ -0.4 to -0.6) recorded are intermediate in value (Robinson, 1986). This indicates that some samples contain either magnetically soft minerals with a fine magnetic domain size or an assemblage with a small canted antiferromagnetic component, or both. Whilst those S-ratio values with low negative S-ratio values ($\leq$-0.7), indicate that some of the samples have a dominance of magnetically soft minerals with a coarse magnetic domain grains. The mean $\chi_{FD\%}$ (4.37%) of the samples can be described as a medium value (Dearing, 1999), indicating an admixture of superparamagnetic and coarser grains. This is supported by the mean χ_{ARM}/SIRM (0.51 x10^{-5} Am^{-1}), indicating that the samples are mainly coarse stable single domain grains (Dearing *et al.*, 1997).

It is generally accepted (Maher, 1986; Maher & Taylor, 1988; Dearing *et al.*, 1996b) that superparamagnetic and stable single domain size grains dominate free-draining surface soils, produced by weathering and/or fermentation processes, and therefore, indicates a possible source for the street dusts. This interpretation is similar to the results observed by Xie *et al.*, (2000) who identified surface soils as being the significant source component of street dusts in the City of Liverpool.

Previous magnetic pedological studies (Dearing *et al.,* 1996b), have shown the mean χ_{LF} and $\chi_{FD\%}$ of top soils to be 7.3 x10^{-7} m^{-3} kg^{-1} and 4.1%, respectively. On this basis, Xie *et al.*, (1999) describe their mean χ_{LF} street dust data (23.7 x10^{-7} m^{-3} kg^{-1}) as being more than two times higher than typical top soils and their mean $\chi_{FD\%}$ data (1.7%) as notably lower than top soils. When our results are compared to both these data, it is apparent that the mean χ_{LF} (58.8 x10^{-7} m^{-3} kg^{-1}) of Road One street dusts are more than eight times higher than typical top soils and twice the concentration of Liverpool street dusts. Liverpool samples were collected from a large variety of locations including city centre areas and residential gardens and roads. The much greater mean χ_{LF} value recorded at Road One when compared to the Liverpool results may be indicative of the higher input of vehicle-derived particulate in Road One. It is also noticeable that the mean $\chi_{FD\%}$ (4.4%) of Road One street dusts is extremely comparable to typical top soils and considerably higher than Liverpool street dusts. This suggests that, in addition to surface soils, Road One street dusts contain a significant contribution of other sources of magnetic minerals (Beckwith *et al.*, 1986).

A large quantity of Fe-rich, spherical, dust particulates were seen in SEM micrographs taken of dust collected from Road One. Since the size of the sphericules observed in the samples (0.2 – 2 μm) is similar to the approximate size of stable single domain and pseudo single domain grains (0.07 to 0.7μm and 0.7 to 10μm, respectively (Smith, 1999) it is plausible to propose that the source of the coarse stable single domain grains can be attributed to a vehicle combustion bi-product, expelled as particulates from the emissions of diesel engines.

Earlier work, in Southern Germany, by Hanesch and Petersen (1999) has determined the magnetic properties of a brown earth soil, where the presence of deposited, combustion generated particles clearly influenced the observed magnetic properties. The authors were able to demonstrate the presence of metallic spherules in the soil horizons using electron microscopy. In this study, it is possible that vehicle derived particles present in the urban street dusts, such as the Fe rich particles observed, could influence the mineral magnetic properties in a similar manner.

Significant correlations were observed between LOI and χ_{LF}, χ_{HF}, $\chi_{FD\%}$, HARD%, or χ_{ARM}/SIRM and insignificant correlations between LOI and SOFT% or S-ratio. Bivariate scatter plots for the most significant correlations of LOI versus $\chi_{FD\%}$ and versus χ_{ARM}/SIRM show the positive linear relations. The significance and strength of these correlations supports the findings of Xie *et al.*, (2000) who noted similar values to those presented in this study. These suggest that surface soils and vehicular derived

particulates may represent an important source of dust organic matter in the West Midlands.

5.14 Pathways of human exposure to vehicle emissions and airborne particulate matter

Elemental, anionic and magnetic measurements of dust have demonstrated likely relationships between indoor settled dust (on floors and surfaces), street dust, surface soil and indoor/outdoor airborne particulate matter. Therefore, the movement of particulate matter can be considered to be occurring through these inter-related spheres, both indoors and outdoors. A qualitative schematic model can be formulated showing plausible pathways of airborne particulate in general and how vehicle emissions could add to the personal exposure of building occupants (Figure 5.1). Experimental results presented in Chapter 3 have provided evidence of several pathways/relationships and these are displayed in a second schematic model (Figure 5.2). This type of schematic model could form the basis of a quantitative numerical model showing the movement of chemical species and particulate mass between the spheres and ultimately aid in calculating possible personal exposure for a given set of circumstances. This model could be further expanded by illustrating the complex physical processes (deposition, re-suspension, surface creep, saltation and aqueous transport), which occur during transition from one phase of dust to another and the factors, meteorology and building use for example, which effect the type of transportation mechanism which is likely to occur. In addition, the type of transport process occurring is largely dependent upon the

size of the particulate material. For example, particles greater than 100 μm in diameter are likely to be transported by saltation or creep, whereas, particles smaller than 10 μm can easily be suspended into the atmosphere. However, the agglomeration of small particles into larger particles and the breakdown of large particles into smaller particles is an important mechanism that would be very difficult to model.

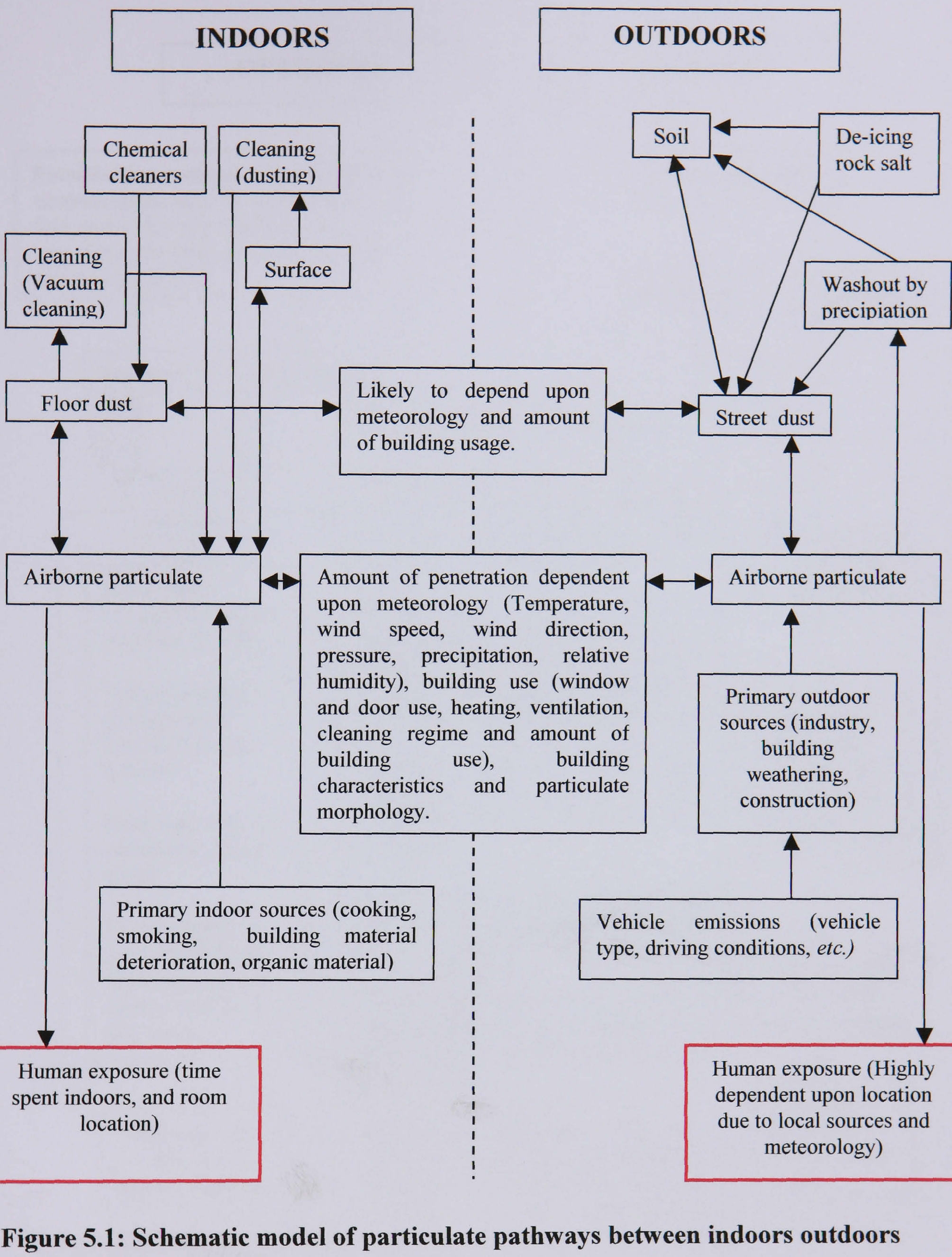


Figure 5.1: Schematic model of particulate pathways between indoors outdoors

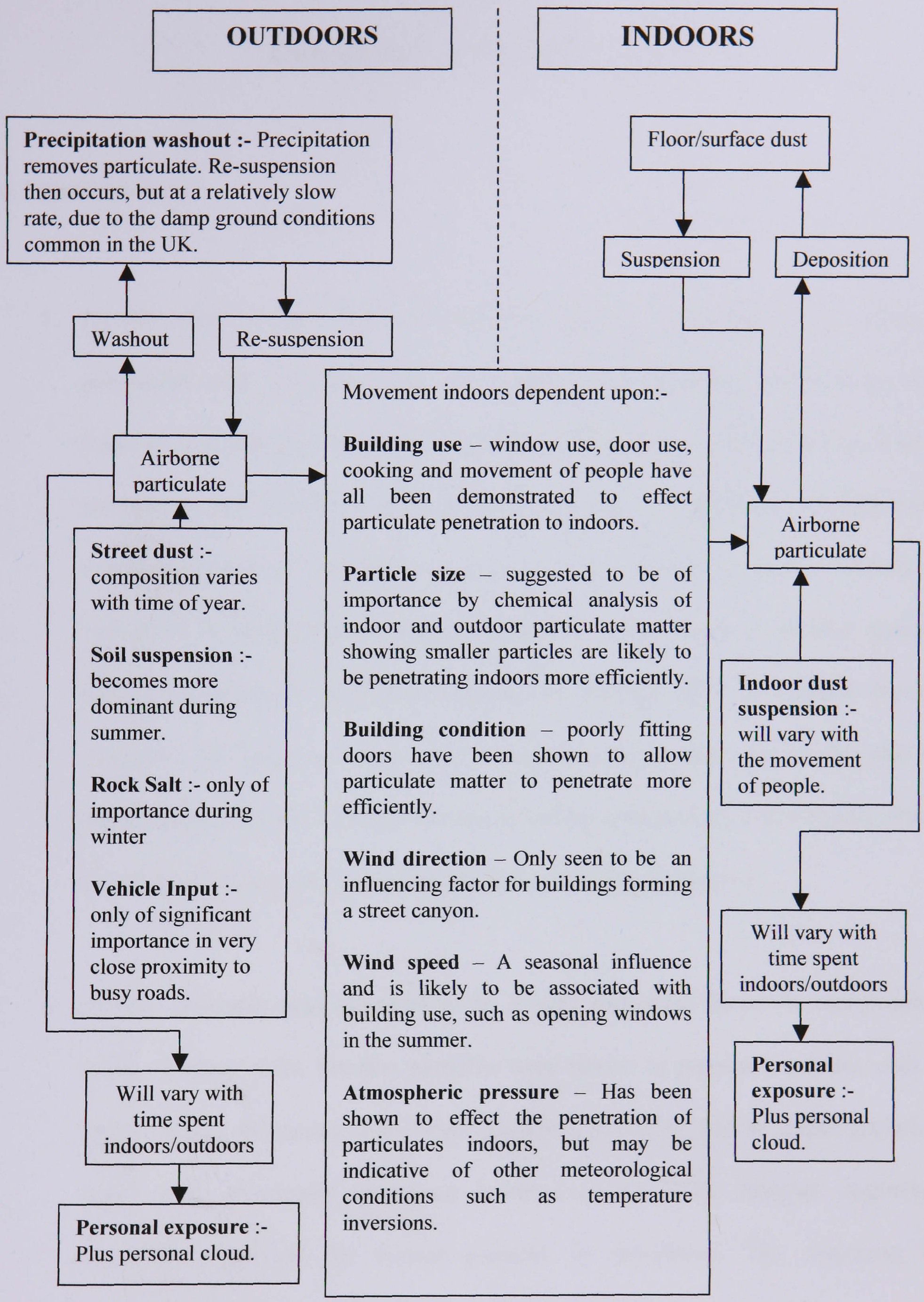


Figure 5.2: Schematic model showing pathways identified by this research

Chapter 6

Conclusions and further work

6.1 Conclusions

1. As expected, outdoor airborne particulate matter concentrations are closely associated with location, with the greatest concentrations observed at the location with the greatest source strength. Indoor and personal exposure levels are significantly correlated with outdoor concentrations, therefore, it is apparent that the location of a building has a direct effect on the exposure of building occupants to air pollutants. The building shell offers some protection against particulate exposure with indoor levels on average 43% of outdoor levels. However, the indoor:outdoor ratio is highly variable from day to day and is significantly affected by many factors including meteorology (wind speed, wind direction, pressure, *etc.*), building use and particulate deposition.

2. Particle diameter was observed to be a very important factor in determining indoor:outdoor ratio. Smaller particles were shown to penetrate indoors with a much greater efficiency than larger particles, probably due to larger particles being more efficiently entrapped in the building shell. Another important removal mechanism for indoor particles is deposition. The reduction in particulate mass from outdoors to indoors may also be partly due to larger particles depositing out of the air, upon penetration indoors, at a rate far greater

than smaller particles. The deposition of these larger particles would not be a significant removal mechanism outdoors due to the relatively high amount of turbulence in ambient air. However, as indoor air is relatively slow moving, large particles would quickly deposit leading to a subsequent decrease in indoor particulate concentration and a lowering of the indoor:outdoor ratio.

3. Meteorology was observed to effect particulate concentrations and penetration both outdoors and indoors. Short term meteorological factors such as precipitation, wind direction and atmospheric pressure were observed to have a noticeable effect upon indoor and outdoor concentrations. However, wind speed significantly effects outdoor concentrations and has no significant effect upon indoor levels. Generally, it has been observed that the relationships that exist between indoor and outdoor particulate concentrations and meteorology are highly complex. This complexity is further demonstrated by alterations in relationships from season to season. Because of this, the modelling of indoor:outdoor particulate relationships would be very difficult to assess requiring extremely intricate algorithms, taking many factors into account. One of the main difficulties involved with modelling indoor and outdoor particulate concentrations to meteorology is that meteorological conditions are closely inter-related. This makes separating the individual effects of each meteorological parameter implicitly difficult.

4. Particle count of sub-micron particles and gravimetric PM_{10} measurements taken with a forward light scattering instrument follow almost identical trends over time, with this relationship observed inside and outside of all buildings. This suggests that in the locations monitored in this research sub-micron particles appear to be originating from the same sources as larger particles in the 1 to 4 μm size range.

5. It appears likely that by using mineral magnetic measurements, certain sources of street dusts may be identified. In this case, the dusts taken from a road with the greatest vehicular particulate input showed a significant difference in magnetic signature. The cause of the variation in magnetic signature is currently unclear, however, it may be due to the input of magnetic minerals in the form of sub-micron spherulites, which may be emitted by vehicles. It is also possible that particles produced by the wear and tear of the vehicle body may be altering the magnetic signature of nearby street dusts.

6. As well as significant differences in magnetic signature, airborne particles and street dust samples from different locations also show varying chemical signatures. It seems likely that certain elements and anions, such as Cu, Zn and sulphate, may be of use as a tracer for vehicle particulate emissions as it is possible they are produced by the combustion of fuel or emitted due to engine wear. It is also clear that certain elements and anions (such as Cu, Zn and

sulphate) can penetrate indoors with a far greater efficiency than others (such as Al, K and chloride).

7. By using chemical analysis of street dust, indoor dust and airborne particulate matter it is possible to make two suggestions. Firstly, it appears that street dust, settled dust and airborne particles in Wolverhampton City Centre, both indoors and outdoors, are generally originating from similar sources. This was shown during winter with a large increase in chloride concentrations in all dust phases. Other evidence to suggest this conclusion is the presence of vehicle related analytes, such as sulphate and Zn, being found in greater concentrations where vehicle input is highest. Secondly, there is movement occurring between these different phases of dust that can be illustrated in a schematic model. Transferral between the phases is occurring through deposition and re-suspension as well as the direct input from primary sources such as vehicle emissions and soil suspension. It is clear that many factors will be effecting this movement and they are generally highly dependent upon location, meteorology, particle diameter and other empirical factors.

8. This research has highlighted the difficulties facing local authorities in the UK, who have a legislative responsibility to declare areas falling below air quality guidelines as Air Quality Management Areas. It is clear from the results obtained in Wolverhampton City Centre that 'hot spots' of air pollution can exist in specific locations that are not recorded at monitoring stations located relatively

closely. These 'hot spots' may be only one short stretch of road so that Gauss dispersion models often utilised by local authorities, such as Cambridge Environmental Research Consultants ADMS (Atmospheric Dispersion Model System) and Indic Airviro, do not identify a problem due to a lack of resolution. For air pollutants such as NO_2, this is not a problem as cheap, low maintenance diffusion tubes can be used for monitoring. However, particulate sampling equipment is often expensive, high maintenance and impractical in many public areas. Therefore, it seems likely that air quality management in the UK will develop into a structured process addressing the most widespread and heavily polluting sources first, such as motorway corridors, arterial roads and certain industries, before attempting to solve air quality problems at small isolated hot spots such as the one identified during this research.

6.2 Suggestions for further work

1. There appears to be other factors affecting the indoor:outdoor ratio that were not identified during this research, possibly associated with the buildings heating and ventilation systems that could not be controlled during monitoring. A logical step to expand upon this section of the research would be to simultaneously record particulate concentrations using real time monitors (outdoor, indoor and personal exposure) at relatively small averaging periods, such as one hour or even 15 minutes. It is possible that measurements at these relatively small time

scales would show short term, high peaks in particulate concentrations, which are missed with an 8 hour average.

2. Shorter averaging periods would improve the understanding of meteorological effects. Due to the dynamic nature of meteorology a relatively large amount of information is lost in a 24 hour average, so that shorter averaging times would identify short term variations.

3. Taking PM_{10} and particle count measurements from a larger variety of locations, both urban and rural, would help to illustrate the degree to which simultaneous PM_{10} and particle count measurements can be used to determine particle sources.

4. A larger amount of samples from a wider variety of locations is required to enable further analysis of spatial and temporal differences, ensuring that the significant difference observed here is not an individual phenomenon.

5. Since this research started (1999), there have been large advances in computer controlled scanning electron microscopy. This equipment is able to count, chemically analyse and measure particles at a rate far higher than is possible using manual methods. Currently, this has been used fairly extensively to characterise particles collected on filter papers. However, it would also be possible to utilise computer controlled scanning electron microscopy to analyse settled dust particles collected on the SEM stubs. This would give a far greater

sample collection and could be combined with computer controlled SEM measurements of airborne particulate matter collected on filter papers. The results from such an experiment could give more information on the movement between settled dust and airborne particulate matter due to the larger number of chemical and morphological measurements.

6. Although Cu, Zn and sulphate can be traced back to vehicle emissions they can also originate from other sources, such as industry. Therefore, a more detailed chemical analysis including organic compounds such as PAHs (known to be present in diesel particulate) may reveal ratios between elements, anions and organic compounds that could be used as more effective tracers for vehicle emissions.

Chapter 7

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Appendix 1

Meteorological data

	Mean Wind Speed (m/s)	Mean Wind Direction (°E from N)	Mean Pressure (Mb)	Total Duration of Rainfall During Sampling (Hours)	Total Quantity of Rainfall (mm)	Mean Relative Humidity (%)
19/09/00	2.5	12.04	966.3	-	-	-
20/09/00	2.6	55.77	966.64	-	-	-
21/09/00	3.61	57.04	976.65	-	-	-
22/09/00	3.35	49.41	980.08	-	-	-
25/09/00	3.68	31.56	980.23	-	-	-
26/09/00	4.48	66.9	973.09	-	-	-
27/09/00	3.84	63.83	968.72	-	-	-
28/09/00	3.68	46.67	963.77	-	-	-
02/10/00	2.66	47.9	969.22	-	-	-
03/10/00	3.45	40.96	975.8	-	-	-
04/10/00	5.28	58.44	973.59	-	-	-
05/10/00	3.47	53.48	972.98	-	-	-
06/10/00	2.85	323	981.85	-	-	-
09/10/00	2.78	35.01	976.27	-	-	-
10/10/00	4.15	61.63	961.82	-	-	-
11/10/00	-	-	-	-	-	-
12/10/00	-	-	-	-	-	-
13/10/00	-	-	-	-	-	-
16/10/00	-	-	-	-	-	-
17/10/00	-	-	-	-	-	84.09
18/10/00	-	-	-	-	-	87.99
19/10/00	-	-	-	-	-	83.1
20/10/00	-	-	-	-	-	93.91
23/10/00	-	-	-	-	-	85.75
24/10/00	-	-	-	-	-	92.33
25/10/00	-	-	-	-	-	80.23
26/10/00	-	-	-	-	-	88.81
27/10/00	-	-	-	-	-	92.54
30/10/00	-	-	-	-	-	95.76
31/10/00	-	-	-	-	-	86.26
01/11/00	3.94	56.42	962.13	5.5	9.4	94.46
02/11/00	3.47	65.6	961.13	1.5	0.6	96.34
03/11/00	3.67	37.1	965.48	15	33.8	93.47
06/11/00	3.43	305.1	961.21	7.5	7.8	99.73
07/11/00	3.69	320	962.5	9	7.2	99.08
09/11/00	3.02	40.81	969.6	1.5	0.8	97.43
10/11/00	4.44	68.4	965.32	9.5	10	94.34
13/11/00	3.09	72.25	962.04	0	0	92.12

14/11/00	1.16	1.28	968.41	0	0	99.4
15/11/00	3.45	52.15	967.81	3.5	2.6	99.97
16/11/00	3.54	61.85	966.59	1	0.4	93.85
17/11/00	3.61	45.44	965.12	6	6.6	97.35
20/11/00	1.96	67.5	961.64	0	0	99.39
21/11/00	4.83	48.19	961.77	14	12.4	100.5
22/11/00	3.16	56.1	961.9	0	0	96.68
23/11/00	2.53	23.19	966.42	4	3	100.31
24/11/00	4.82	64.65	963.2	10.5	11.2	96.15
27/11/00	3.95	63.96	971.22	7.5	10	100.5
28/11/00	5.75	62.27	963.73	0.5	0.2	94.03
29/11/00	4.89	67.67	966.61	0	0	93.01
30/11/00	5.11	58.13	968.13	4.5	2.2	97.94
01/12/00	4.29	64.63	970.01	8	9.8	97.31
05/12/00	4.96	63.67	964.12	7	23.2	100.09
06/12/00	3.39	53.92	964.83	1.5	1.8	99.57
07/12/00	6.75	32.92	961.87	10	17.8	99.11
08/12/00	5.76	69.17	967.87	13.5	17	97.23
11/12/00	4.29	67.46	967.76	1	0.4	100.1
12/12/00	7.38	66.67	962.63	5.5	8.6	86.96
13/12/00	4.28	66.67	963.82	0.5	0.2	94.13
14/12/00	1.65	339.19	968.21	3	2.4	99.04
15/12/00	1.32	35.17	969.84	0.5	0.2	98.02
18/12/00	3.15	7.4	978	1.5	1.6	100.5
19/12/00	4.04	41.37	972.13	2	1.2	100.5
20/12/00	-	-	-	-	-	99.02
04/01/01	1.88	30.23	961.15	0	0	-
05/01/01	3.28	55.28	964.85	0	0	92.58
08/01/01	2.53	189.46	968.54	0	0	91.54
10/01/01	6.64	321.29	972.80	0	0	82.39
11/01/01	6.43	343.33	982.18	0	0	-
12/01/01	3.49	352.94	990.83	0	0	92.3
15/01/01	2.51	355.58	979.46	0	0	98.28
16/01/01	2.30	359.67	978.59	0	0	98.28
17/01/01	1.52	3.58	978.00	0	0	92.41
18/01/01	0.51	14.48	976.06	0	0	90.61
19/01/01	2.49	125.37	978.94	7	7.2	98.5
06/02/01	6.88	70.60	961.51	1.5	1	74.87
07/02/01	3.45	347.27	961.21	0	0	77.63
08/02/01	1.98	314.29	961.42	0	0	70.76
09/02/01	4.85	51.37	980.02	19.5	21.2	85.14
13/02/01	0.73	24.75	977.47	0	0	80.14
14/02/01	1.15	32.90	974.57	0	0	74.09
15/02/01	1.17	239.31	987.65	1.5	0.6	90.14
19/02/01	1.24	341.15	986.35	0	0	-
20/02/01	2.64	13.63	975.45	0	0	92.74
21/02/01	2.57	297.63	976.27	1.5	0.6	96.09
22/02/01	3.76	302.23	967.32	2	0.8	92.06

23/02/01	2.94	204.15	966.39	1.5	0.8	81.29
26/02/01	2.32	32.42	962.38	3	2	99.9
27/02/01	2.63	301.29	964.80	3	2.8	99.88
28/02/01	3.61	293.94	962.32	0	0	92.78
01/03/01	2.62	328.99	962.54	0	0	76.1
05/03/01	3.21	35.60	968.05	0	0	75.44
06/03/01	5.36	45.00	967.66	4	5.8	86.22
07/03/01	3.57	63.35	962.88	0	0	93.13
08/03/01	3.38	65.50	961.65	1	0.4	94.37
09/03/01	3.49	68.23	963.42	4	3.2	95.44
27/03/01	3.4	51.1	967.1	5.5	8	-
28/03/01	1.71	325.12	961.40	0	0	-
29/03/01	3.85	46.40	968.64	2.5	2.2	79.9
02/04/01	2.9	62.18	966.33	5	5.6	94.53
03/04/01	4.1	22.89	967.07	12	14	77.45
04/04/01	4.01	38.97	965.32	4.5	9.8	85.79
05/04/01	5.29	57.58	962.57	2.5	2.2	98.41
06/04/01	3.34	12.45	969.60	12	15.4	86.5
09/04/01	4.40	0.58	967.06	1.5	1.4	86.96
10/04/01	3.33	291.37	976.68	2.5	1.6	90.54
24/04/01	3.05	57.27	963.54	5.5	6.4	-
27/04/01	2.04	15.73	967.48	7.5	8.2	-
30/04/01	2.57	299.39	970.47	0	0	-
01/05/01	2.46	331.41	975.72	0	0	-
02/05/01	1.13	312.12	970.59	0	0	-
03/05/01	2.22	300.75	969.19	0	0	48.4
04/05/01	1.01	313.84	983.19	0	0	58.11
08/05/01	3.32	328.83	978.40	0	0	81.77
09/05/01	2.61	337.94	975.50	11	15.4	65.4
14/05/01	3.13	314.06	972.20	6.5	13	77.75
16/05/01	-	-	-	-	-	67.8
17/05/01	-	-	-	-	-	91
18/05/01	-	-	-	-	-	76.34
21/05/01	-	-	-	-	-	90.06
22/05/01	-	-	-	-	-	59
23/05/01	-	-	-	-	-	50.67
24/05/01	-	-	-	-	-	77
29/05/01	-	-	-	-	-	68.10
30/05/01	-	-	-	-	-	74.4
31/05/01	-	-	-	-	-	69
04/06/01	-	-	-	-	-	63.04
05/06/01	-	-	-	-	-	74
07/06/01	-	-	-	-	-	61.55
08/06/01	-	-	-	-	-	66
11/06/01	-	-	-	-	-	69.32
12/06/01	-	-	-	-	-	53.58
13/06/01	-	-	-	-	-	72
15/06/01	-	-	-	-	-	92

18/06/01	2.67	66.56	976.12	0	0	-
19/06/01	4.09	59.66	970.89	0	0	-
20/06/01	2.97	304.45	969.50	0	0	-
22/06/01	3.31	16.12	971.10	0	0	-
25/06/01	2.99	20	970.63	0	0	-
26/06/01	3.70	54.77	966.14	0	0	-
27/06/01	3.97	66.75	966.42	0	0	-
28/06/01	3.60	63.12	963.86	0.8	1.5	-
02/07/01	2.32	58.70	970.70	0	0	-
04/07/01	3.75	333.52	969.55	0	0	-
05/07/01	3.59	335.20	969.42	0	0	-
09/07/01	2.94	67.45	968.55	0	0	-
10/07/01	5.55	57.02	964.27	3	3	-
11/07/01	5.12	56.66	963.35	0.2	0.5	-
13/07/01	1.77	298.91	963.21	1	0.5	-
16/07/01	2.85	25.79	965.21	0	0	-
18/07/01	4.67	292.77	964.70	0.8	2	-
23/07/01	2.47	31.04	969.98	0	0	-
24/07/01	1.42	343.47	971.05	0	0	-
25/07/01	1.87	3.54	971.97	0	0	-
27/07/01	1.34	303.45	972.02	0	0	-
30/07/01	2.47	1.62	973.73	0.2	0.5	-
31/07/01	1.88	316.75	975.99	0	0	-
01/08/01	2.01	23.77	972.28	0	0	-
02/08/01	1.92	6.72	970.71	1.4	3.5	-
07/08/01	3.98	44.33	963.95	1.2	1	-
08/08/01	1.91	289.64	966.16	1.2	1	-
09/08/01	3.61	291.25	972.56	0.2	0.5	-
14/08/01	1.92	51.62	968.55	0.4	0.5	-
15/08/01	2.47	340.16	970.39	9.8	5	-
16/08/01	3.12	67.70	972.79	4.6	1.5	-
21/08/01	2.54	99.62	974.42	0	0	-
22/08/01	0.83	95	974.52	0	0	-
04/09/01	3.06	180.10	972.40	0	0	-

Appendix 2

Indoor and outdoor respirable particulate measurements for Building One

Date of Sample	Outdoor $\mu g\ m^{-3}$	Indoor $\mu g\ m^{-3}$	I:O Ratio
19/09/00	13	11	0.84
20/09/00	8	2	0.27
21/09/00	47	12	0.25
22/09/00	14	13	0.91
25/09/00	15	10	0.66
26/09/00	9	4	0.41
27/09/00	41	14	0.34
28/09/00	15	9	0.57
10/02/00	17	2	0.12
10/03/00	20	9	0.43
10/04/00	22	19	0.86
10/05/00	16	9	0.56
10/06/00	12	26	2.12
10/09/00	19	5	0.27
10/10/00	14	3	0.20
10/11/00	17	7	0.44
10/12/00	26	7	0.26
13/10/00	15	3	0.21
16/10/00	19	7	0.37
17/10/00	17	3	0.17
18/10/00	25	6	0.24
19/10/00	29	5	0.19
20/10/00	28	6	0.22
23/10/00	14	3	0.17
24/10/00	11	3	0.24
25/10/00	18	4	0.23
26/10/00	20	8	0.41
27/10/00	5	1	0.19
30/10/00	11	2	0.22
31/10/00	16	6	0.34
11/01/00	6	6	1.00
11/02/00	18	8	0.42
11/03/00	25	2	0.08
11/06/00	11	1	0.09
11/07/00	-	7	-
11/09/00	-	14	-
11/10/00	-	7	-

13/11/00	23	11	0.47
14/11/00	-	19	-
15/11/00	-	12	-
16/11/00	29	14	0.47
17/11/00	20	6	0.28
20/11/00	37	12	0.33
21/11/00	44	19	0.43
22/11/00	32	12	0.39
23/11/00	22	14	0.66
24/11/00	20	7	0.35
27/11/00	20	14	0.69
28/11/00	10	5	0.47
29/11/00	31	17	0.53
30/11/00	23	17	0.75
12/01/00	22	5	0.21
12/05/00	25	8	0.31
12/06/00	24	9	0.38
12/07/00	25	15	0.59
12/08/00	19	6	0.32
12/11/00	19	14	0.70
12/12/00	11	7	0.65
13/12/00	13	8	0.61
14/12/00	17	13	0.74
15/12/00	35	12	0.34
18/12/00	51	19	0.37
19/12/00	38	14	0.37
20/12/00	34	18	0.53
01/04/01	31	12	0.39
01/05/01	18	6	0.33
01/08/01	43	10	0.23
01/10/01	16	12	0.74
01/11/01	-	-	-
01/12/01	19	2	0.11
15/01/01	51	20	0.39
16/01/01	66	18	0.27
17/01/01	97	18	0.19
18/01/01	110	22	0.20
19/01/01	59	6	0.11
02/06/01	-	13	-
02/07/01	32	15	0.46
02/08/01	21	14	0.65
02/09/01	21	6	0.28
13/02/01	24	-	-
14/02/01	-	17	-
15/02/01	54	8	0.15
19/02/01	49	13	0.27
20/02/01	25	13	0.51
21/02/01	17	14	0.84

22/02/01	16	9	0.56
23/02/01	27	14	0.50
26/02/01	30	14	0.46
27/02/01	25	12	0.49
28/02/01	33	10	0.31
03/01/01	29	7	0.23
03/05/01	89	20	0.23
03/06/01	41	19	0.46
03/07/01	33	7	0.22
03/08/01	25	12	0.48
03/09/01	16	5	0.31
27/03/01	45	29	0.64
28/03/01	30	15	0.51
29/03/01	23	6	0.24
04/02/01	40	14	0.35
04/03/01	15	12	0.76
04/04/01	30	15	0.49
04/05/01	34	11	0.33
04/06/01	27	5	0.19
04/09/01	26	12	0.45
04/10/01	16	15	0.93
24/04/01	43	-	-
27/04/01	29	6	0.20
30/04/01	22	10	0.46
05/01/01	8	8	1.00
05/02/01	33	12	0.35
05/03/01	-	10	-
05/04/01	50	6	0.11
05/08/01	36	2	0.04
05/09/01	44	5	0.10
14/05/01	38	22	0.56
16/05/01	13	3	0.22
17/05/01	17	4	0.20
18/05/01	-	-	-
21/05/01	-	-	-
22/05/01	30	11	0.36
23/05/01	40	22	0.54
24/05/01	-	6	-
29/05/01	30	13	0.45
30/05/01	66	7	0.11
31/05/01	-	2	-
04/06/01	-	15	-
05/06/01	34	4	0.12
07/06/01	19	11	0.57
08/06/01	31	7	0.24
11/06/01	25	11	0.45
12/06/01	13	15	1.18
13/06/01	59	9	0.16

15/06/01	35	4	0.12
18/06/01	-	11	-
19/06/01	22	8	0.35
20/06/01	19	7	0.35
22/06/01	23	7	0.29
25/06/01	-	19	-
26/06/01	63	16	0.26
27/06/01	20	13	0.68
28/06/01	-	4	-
02/07/01	32	12	0.37
04/07/01	-	16	-
05/07/01	60	9	0.15
09/07/01	30	17	0.56
11/07/01	-	19	-
11/11/01	26	10	0.39
13/07/01	21	10	0.45
16/07/01	39	11	0.29
18/07/01	20	6	0.32
23/07/01	16	8	0.51
24/07/01	20	14	0.69
25/07/01	34	13	0.39
27/07/01	29	11	0.40
30/07/01	8	15	1.78
31/07/01	26	19	0.71
01/08/01	43	20	0.48
02/08/01	35	21	0.61
07/08/01	22	15	0.70
08/08/01	11	14	1.22
09/08/01	10	29	3.00
14/08/01	34	19	0.58
15/08/01	19	50	2.67
16/08/01	15	13	0.85
21/08/01	21	17	0.82
22/08/01	40	21	0.52
04/09/01	5	17	3.25

Appendix 3

Indoor and outdoor respirable particulate chemical analysis

Indoor and outdoor anion concentrations

Concentrations in ng m^{-3}

	INDOOR			OUTDOOR		
Date	**Sulphate**	**Nitrate**	**Chloride**	**Sulphate**	**Nitrate**	**Chloride**
19/09/00	3783	803	268	674	433	572
21/09/00	3128	686	465	7335	3429	444
25/09/00	2407	582	191	9105	4395	372
27/09/00	3863	1098	553	1042	316	629
10/02/00	440	193	145	5485	1695	345
10/04/00	4392	1795	1199	4848	1351	465
10/06/00	6323	2442	1648	3370	1205	292
10/10/00	613	152	107	6451	2108	1001
10/12/00	1470	454	308	2512	799	568
16/10/00	1742	388	125	867	463	686
18/10/00	1744	451	261	2757	891	514
20/10/00	1531	386	120	2455	873	729
24/10/00	582	243	43	2840	979	247
26/10/00	1814	776	366	2790	644	1551
30/10/00	703	209	73	1180	309	1773
01/11/00	1883	339	201	3183	1716	426
03/11/00	584	171	13	916	438	657
16/11/00	4714	1140	832	4157	1491	440
20/11/00	3380	815	277	2547	1081	577
22/11/00	2700	697	335	8202	2098	553
24/11/00	1534	618	115	4901	1800	454
28/11/00	1408	352	81	2449	619	377
30/11/00	5779	1006	769	8148	1780	1217
05/12/00	1398	217	441	2785	1720	806
07/12/00	3726	342	380	6011	402	613
11/12/00	2843	754	267	3175	495	819
13/12/00	1469	173	433	4151	592	765
15/12/00	1966	467	754	4563	818	1157
19/12/00	2689	600	618	2727	732	925
04/01/01	2679	814	386	4983	1535	695
08/01/01	1126	388	529	2213	1420	810
15/01/01	3168	876	1057	5544	1679	304
17/01/01	4913	1403	747	6027	2657	954
19/01/01	417	143	302	632	433	622
07/02/01	3800	708	269	5271	2254	610
09/02/01	229	21	78	1298	2048	408

19/02/01	3383	935	534	5362	1377	948
21/02/01	4033	844	334	7279	8	551
23/02/01	3191	583	774	6125	1461	1004
27/02/01	3114	809	237	4922	3475	510
01/03/01	2108	494	187	3268	1802	467
06/03/01	4510	1819	1302	6810	1487	1448
08/03/01	3132	801	390	5042	973	602
27/03/01	7611	2133	650	11340	4459	1069
29/03/01	1612	440	302	2596	832	590
03/04/01	2705	851	635	4599	1274	920
05/04/01	2427	638	709	3811	1135	985
09/04/01	2516	670	606	3649	1915	976
30/04/01	2276	518	215	3755	1232	521
02/05/01	2524	899	695	4316	1996	868
04/05/01	1663	491	169	2711	934	504
09/05/01	1190	307	47	1917	641	336
16/05/01	747	182	91	1098	352	385
22/05/01	2338	1015	220	3530	2131	549
30/05/01	1799	401	308	3059	1312	625
07/06/01	3603	807	234	5260	1484	568
06/06/01	3662	594	172	5456	823	523
11/06/01	2006	724	329	2889	1573	623
20/06/01	2119	362	180	3391	728	591
27/06/01	4534	811	583	6755	1776	1064
02/07/01	3447	586	634	5170	1266	1163
05/07/01	2221	486	104	3442	966	518
13/07/01	2795	740	497	4136	1884	946
18/07/01	1639	544	57	2787	2191	382
24/07/01	3542	868	637	5136	1354	996
27/07/01	3890	978	143	6730	1192	525
31/07/01	3772	948	958	5846	1725	524
02/08/01	4257	2107	1017	6215	3687	730
08/08/01	3007	710	674	5172	1363	302
14/08/01	6212	1941	17	8883	3638	726
16/08/01	3090	961	513	4481	3688	343
22/08/01	4869	1935	282	6865	1979	553

Indoor elemental concentrations

Concentrations in ng m^{-3}									
Date	**Al**	**Ca**	**Cu**	**Fe**	**K**	**Mg**	**Mn**	**Pb**	**Zn**
20/09/00	6.27	11.92	2.25	63.18	18.98	61.00	5.37	97.29	5.48
22/09/00	9.22	27.10	39.97	52.44	5.94	92.04	5.05	75.03	68.79
26/09/00	5.70	10.76	12.30	45.00	5.67	69.03	19.98	61.57	4.81
28/09/00	16.64	21.60	24.76	70.00	19.04	39.90	7.51	83.78	28.30
03/10/00	15.35	16.88	33.41	45.36	10.26	38.40	13.39	103.35	55.42
05/10/00	7.94	19.86	18.65	64.75	20.30	96.99	23.51	94.08	28.68
09/10/00	16.55	2.12	4.84	48.24	14.40	81.84	21.76	96.39	6.76

11/10/00	5.50	27.31	65.21	69.92	17.28	56.33	6.27	64.86	35.84
13/10/00	3.25	6.77	11.44	71.04	13.30	58.46	25.56	106.26	3.20
17/10/00	29.56	7.83	6.76	73.10	35.00	77.90	21.07	84.00	9.25
19/10/00	1.33	11.05	4.58	49.00	8.55	78.00	3.21	70.65	9.58
23/10/00	21.32	51.05	10.87	42.84	19.80	87.98	6.83	91.54	12.35
25/10/00	4.76	57.56	22.24	57.35	5.67	79.05	23.92	76.95	17.65
27/10/00	10.71	6.59	1.58	35.76	27.52	79.80	2.66	72.48	3.42
31/10/00	14.96	30.93	4.45	58.20	6.30	97.96	6.49	121.04	12.87
02/11/00	2.33	7.55	3.31	34.32	33.60	54.06	27.26	88.36	6.75
06/11/00	21.89	36.36	8.03	53.32	27.90	74.97	4.16	64.37	4.92
09/11/00	9.58	20.84	66.53	65.86	10.64	54.45	5.33	115.94	74.37
13/11/00	20.24	47.53	13.99	50.40	21.12	78.54	12.29	61.18	14.65
15/11/00	11.58	8.37	33.74	39.00	9.52	46.00	58.66	62.10	33.37
17/11/00	19.03	14.21	10.31	67.32	19.04	41.58	5.97	92.40	11.89
21/11/00	19.53	3.65	24.81	59.50	14.55	66.50	24.73	101.84	65.96
23/11/00	65.26	6.51	70.87	60.06	7.56	61.05	5.72	90.18	66.81
27/11/00	15.72	1.16	14.79	58.90	36.10	62.83	17.82	95.15	58.55
29/11/00	67.63	14.29	15.71	39.56	22.08	66.08	10.55	58.75	60.87
01/12/00	9.30	22.53	13.82	41.79	29.58	73.80	7.42	75.79	7.05
06/12/00	22.70	10.60	75.26	45.84	10.08	50.75	10.46	88.40	52.02
08/12/00	19.32	20.65	39.21	71.55	17.28	124.80	3.38	106.76	33.60
12/12/00	14.24	9.18	5.63	29.60	7.52	65.52	7.29	61.16	16.93
14/12/00	20.81	23.38	70.12	43.92	12.32	63.69	1.61	112.86	46.51
18/12/00	79.52	8.64	35.91	54.72	12.60	51.43	17.90	77.44	27.09
20/12/00	49.83	21.63	9.36	33.12	19.88	54.99	17.18	82.80	20.08
05/01/01	9.82	18.07	7.52	61.20	24.50	120.12	2.85	90.63	12.59
10/01/01	39.13	34.87	79.57	48.84	6.44	62.73	22.60	112.45	43.77
12/01/01	5.04	10.25	38.58	42.12	11.28	84.79	16.19	99.68	9.92
16/01/01	64.66	17.44	26.32	36.74	13.92	67.47	52.86	102.66	42.59
18/01/01	46.31	19.50	30.62	60.68	32.80	50.40	10.57	124.20	79.24
06/02/01	34.79	3.08	36.81	62.37	25.48	36.63	25.09	82.56	31.31
08/02/01	47.83	11.38	3.35	53.96	22.10	114.56	10.08	78.20	42.65
15/02/01	7.73	19.47	51.00	50.00	20.52	89.10	19.71	82.80	16.76
20/02/01	16.73	16.59	46.81	41.58	12.78	47.52	19.19	113.85	54.05
22/02/01	26.73	16.87	15.76	61.25	16.80	69.62	15.57	75.04	50.47
26/02/01	48.78	40.90	27.22	62.78	19.44	47.32	4.83	76.68	44.54
28/02/01	17.41	32.74	30.43	43.50	28.80	104.96	17.55	111.54	16.59
05/03/01	57.21	29.79	42.51	53.30	35.28	81.22	15.56	66.69	40.97
07/03/01	27.77	10.51	7.24	29.20	3.64	74.88	29.08	77.40	9.66
09/03/01	13.67	6.30	12.42	39.96	18.24	130.68	5.83	52.46	29.71
28/03/01	20.07	20.67	52.99	47.88	13.16	34.98	27.36	110.88	41.43
02/04/01	31.39	27.00	21.66	63.57	23.70	111.54	21.07	82.35	25.06
04/04/01	15.86	52.42	10.08	55.97	2.75	28.62	25.79	66.78	21.02
06/04/01	25.16	15.75	35.58	50.88	5.76	55.77	11.31	118.32	34.94
10/04/01	23.85	44.45	25.50	44.16	10.27	71.69	32.14	107.46	21.59
27/04/01	15.74	20.70	14.38	39.25	23.25	110.88	38.92	88.69	23.28
01/05/01	27.59	7.34	9.75	53.48	10.45	46.20	6.80	100.44	20.72
03/05/01	25.39	14.39	18.69	44.88	24.49	102.90	6.87	53.55	31.27

08/05/01	11.59	4.52	15.43	33.00	16.20	29.16	3.78	81.18	2.62
14/05/01	30.54	62.22	37.46	40.80	16.60	37.95	26.43	107.25	71.41
17/05/01	65.45	15.12	5.84	52.36	23.80	59.40	2.16	58.88	10.97
23/05/01	47.76	46.40	43.11	79.95	6.09	75.90	10.52	63.75	78.95
29/05/01	34.46	20.65	15.73	33.00	3.95	55.64	25.14	114.00	42.53
31/05/01	48.24	6.41	14.09	75.03	6.60	47.73	16.65	74.80	9.15
05/06/01	41.32	23.76	9.07	78.54	21.12	36.75	17.28	94.87	67.79
08/06/01	22.35	8.74	11.43	45.36	26.32	43.00	36.64	131.60	6.46
12/06/01	52.53	45.31	32.10	56.78	12.35	77.14	12.04	61.50	26.75
15/06/01	42.86	17.91	26.52	72.15	10.88	51.60	21.63	65.19	13.38
19/06/01	41.77	18.14	21.97	50.16	8.46	45.08	26.23	94.50	26.53
22/06/01	56.14	7.10	13.13	72.54	16.50	80.37	8.52	84.50	73.97
26/06/01	21.65	41.16	40.90	79.20	15.00	88.83	7.25	102.96	19.23
28/06/01	52.97	11.91	3.79	60.27	19.50	82.15	40.19	78.75	25.96
04/07/01	17.09	15.23	6.66	36.00	21.78	72.54	10.37	118.34	16.79
09/07/01	38.49	25.83	35.62	51.48	11.52	64.05	11.93	117.81	57.24
11/07/01	39.86	29.08	64.07	70.40	24.42	72.68	36.03	102.12	48.17
16/07/01	4.51	8.81	22.53	32.56	8.16	85.15	17.79	109.20	10.74
23/07/01	25.62	12.64	56.73	38.61	34.32	86.25	12.51	79.73	18.30
25/07/01	57.02	6.41	27.63	53.63	22.57	58.50	32.46	108.60	28.40
30/07/01	2.19	23.76	31.41	43.00	28.48	54.00	2.89	87.10	150.78
01/08/01	6.77	8.74	24.13	57.20	32.40	132.00	11.77	75.60	55.68
07/08/01	9.89	45.31	12.16	31.40	19.11	44.46	17.01	133.70	26.25
09/08/01	29.58	17.91	19.16	55.20	16.66	32.34	21.65	58.56	163.75
15/08/01	13.16	18.14	38.13	80.10	6.93	52.65	6.28	54.61	22.47
21/08/01	23.02	52.18	14.47	43.75	6.02	95.22	6.52	64.40	105.75
04/09/01	10.95	22.77	57.86	71.41	12.00	85.80	4.31	85.20	45.22

Outdoor elemental concentrations

Concentrations in ng m^{-3}									
Date	**Al**	**Ca**	**Cu**	**Fe**	**K**	**Mg**	**Mn**	**Pb**	**Zn**
20/09/00	36.85	42.58	2.917	162	73	122	13.77	141	8.839
22/09/00	126.5	80.05	61.49	138	99	177	20.21	183	104.2
26/09/00	50.35	48.21	3.535	180	63	177	47.57	131	7.07
28/09/00	63.42	80.83	42.69	200	56	114	53.61	142	47.97
03/10/00	72.32	76.28	41.77	168	54	192	78.75	159	80.32
05/10/00	201.9	99.64	13.3	175	58	159	75.83	196	41.57
09/10/00	50.12	66.06	7.926	134	48	186	47.3	153	12.99
11/10/00	66.91	63.21	86.94	184	72	131	52.23	141	76.27
13/10/00	53.43	52.87	2.365	192	95	158	59.43	161	6.956
17/10/00	21.19	17.32	15.37	170	100	190	43.91	120	14.92
19/10/00	91.23	69.19	8.643	140	95	130	14.61	157	23.36
23/10/00	47.91	38.77	20.52	153	60	166	52.53	199	18.16
25/10/00	69.1	27.8	35.3	155	81	155	61.35	135	28.02
27/10/00	24.76	16.64	2.594	149	86	140	9.488	151	5.519
31/10/00	48.43	56.62	9.076	194	90	158	38.16	178	21.11
02/11/00	167.2	69.21	7.036	143	96	106	64.92	188	14.36

06/11/00	19.02	42.98	12.55	172	93	119	27.73	157	10.04
09/11/00	326.3	180.4	98.43	178	56	121	122.2	187	109.4
13/11/00	99.01	76.49	29.59	140	64	154	45.95	133	29.29
15/11/00	100.3	70.09	35.7	195	68	184	33.32	138	77.61
17/11/00	123.3	108.4	18.43	153	68	154	81.95	165	29.73
21/11/00	162	71.74	120.6	170	97	190	57.52	152	103.1
23/11/00	144.7	79.99	105.6	182	84	185	21.2	167	107.8
27/11/00	112.3	43.29	18.4	190	95	103	38.75	173	83.65
29/11/00	270.5	173.3	121.7	172	92	112	105.5	125	117.1
01/12/00	46.52	21.17	13.93	199	87	164	57.1	143	17.63
06/12/00	227	248.3	34.94	191	48	145	69.72	170	77.65
08/12/00	71.57	42.31	56.83	159	72	195	24.12	157	49.42
12/12/00	67.81	22.38	7.604	148	94	168	29.15	139	24.53
14/12/00	109.5	38.1	155.8	183	77	193	14.62	171	116.3
18/12/00	441.8	222	71.81	171	84	139	41.64	176	62.99
20/12/00	453	319.8	17.03	144	71	117	132.1	180	43.66
05/01/01	65.5	32.96	16	153	98	182	10.98	171	26.24
10/01/01	195.6	79.3	127.6	148	92	153	49.14	173	91.18
12/01/01	45.8	37.74	5.67	156	47	139	42.61	178	14.17
16/01/01	239.5	246.7	87.93	167	58	173	132.2	177	68.7
18/01/01	178.1	122.6	114.2	164	82	105	96.07	180	134.3
06/02/01	267.6	226.3	28.65	189	98	111	69.69	129	53.06
08/02/01	251.8	123	48.84	142	85	179	77.52	170	68.79
15/02/01	77.26	81.13	34.18	125	57	165	65.72	180	32.87
20/02/01	139.4	127.6	41.38	126	71	132	45.69	165	84.45
22/02/01	140.7	48.21	46.02	175	80	118	48.66	112	74.22
26/02/01	195.1	113.6	36.29	146	81	182	40.22	142	82.48
28/02/01	116.1	102.3	46.81	145	96	143	73.11	169	36.86
05/03/01	542.1	469.4	98.87	130	98	107	62.24	117	89.07
07/03/01	120.7	65.67	9.656	146	52	198	76.52	180	23.55
09/03/01	65.09	28.64	15.73	148	96	105	23.32	122	43.69
28/03/01	170.2	172.3	98.64	126	94	147	78.18	198	98.64
02/04/01	128.4	128.6	39.39	163	79	108	42.14	183	39.78
04/04/01	206.9	158.8	13.8	193	55	115	64.48	126	31.37
06/04/01	61.39	92.66	55.59	159	64	164	35.34	174	52.95
10/04/01	352.8	262.4	10.79	184	79	131	110.8	199	46.93
27/04/01	154.4	115	24.8	157	75	117	82.8	181	50.6
01/05/01	125.6	66.71	19.91	191	55	198	45.35	162	40.63
03/05/01	103.7	41.1	32.22	187	79	159	42.93	119	47.38
08/05/01	22.75	32.25	2.982	165	81	169	37.8	198	5.232
14/05/01	172.7	163.7	130.5	136	83	106	62.94	195	111.6
17/05/01	41.15	40.88	12.42	154	68	180	12.72	128	20.7
23/05/01	565.7	272.9	143.2	195	87	120	70.56	125	112.8
29/05/01	228.1	79.43	34.19	165	79	196	22.24	190	83.4
31/05/01	15.63	45.79	17.62	183	55	171	35.66	110	13.66
05/06/01	48.35	62.52	14.17	187	48	141	44.76	179	26.24
08/06/01	76.09	67.2	25.4	168	88	155	61.85	188	37.9
12/06/01	211.3	137.3	126.3	167	98	186	48.31	123	113.8

15/06/01	65.8	52.67	16.31	185	77	138	34.33	123	29.13
19/06/01	79.37	50.4	37.87	152	86	107	13.06	175	42.55
22/06/01	52.16	50.73	32.01	186	48	111	43.83	130	39.04
26/06/01	374.3	242.1	186.8	198	61	147	69.84	198	165.4
28/06/01	77.32	45.79	5.257	147	89	172	53.7	175	10.95
04/07/01	137.5	127	10.4	144	81	133	72.01	194	49.54
09/07/01	159.4	103.3	71.24	143	91	200	91.59	187	127.2
11/07/01	182.6	211.4	98.57	176	88	117	70.84	148	74.11
16/07/01	142.5	78.55	15.2	148	94	147	45.06	168	26.2
23/07/01	117.6	98.61	12.38	143	95	195	65.57	119	26.91
25/07/01	268.6	173.9	77.81	173	64	138	85.23	181	56.8
30/07/01	186.3	87.58	30.79	172	94	156	55.78	134	41.61
01/08/01	298.3	171.1	74.18	130	50	183	98.03	189	157.8
07/08/01	155.4	38.29	29.26	157	75	158	35.76	191	88.66
09/08/01	242.4	97.26	77.71	184	75	131	23.86	122	277.5
15/08/01	985.1	221.7	58.78	178	99	125	109.2	127	255.6
21/08/01	156.6	130.8	59.27	175	72	195	80.88	115	89.81
04/09/01	268	174.2	31.34	193	74	100	96.21	142	39.17

Appendix 4

Street dust chemical analysis

The data for Road One are displayed. All the results can be supplied if requested.
All concentrations in $\mu g\ g^{-1}$

0-63 microns									
Sample	**Al**	**Ca**	**Cu**	**Fe**	**K**	**Mg**	**Mn**	**Pb**	**Zn**
MA1	295.60	135.50	13.68	410.67	100.21	54.65	22.47	29.31	31.81
MA2	284.80	288.08	24.04	417.74	79.46	58.27	33.32	11.29	36.42
MA3	275.18	282.92	23.08	294.22	84.76	47.49	23.94	23.07	32.51
MA4	378.44	368.56	12.08	325.06	138.13	50.72	12.49	17.61	21.57
MA5	224.68	162.67	17.77	320.91	33.03	55.73	21.57	11.93	24.02
MA6	332.71	175.77	11.01	219.78	142.40	57.70	40.92	26.99	33.35
JN7	200.37	320.73	28.42	447.83	83.15	47.86	7.81	25.58	35.97
JN8	382.31	309.63	8.31	273.89	178.16	41.98	33.64	25.43	28.65
JN9	350.77	276.83	7.24	131.17	154.69	42.45	22.80	18.82	20.69
JN10	235.68	309.49	11.88	129.41	112.89	48.83	19.33	19.73	25.83
JN11	218.49	361.74	20.88	391.45	96.79	66.68	19.45	20.45	29.41
JN12	389.13	119.77	18.01	162.52	70.43	74.65	31.13	26.40	21.44
JU13	219.95	181.13	7.35	300.25	99.64	76.48	26.83	28.70	36.75
JU14	334.90	237.60	26.72	330.43	154.05	46.31	21.10	23.39	46.87
JU15	374.57	346.25	12.09	369.83	102.26	53.94	34.09	26.80	31.00
JU16	327.70	361.20	14.63	433.71	116.99	61.10	17.04	12.09	33.26
JU17	288.89	186.93	35.11	675.39	131.44	53.63	35.53	26.05	43.35
JU18	275.56	148.56	22.96	228.07	109.40	40.86	9.92	24.50	38.92
AU19	288.99	244.92	16.38	286.91	132.65	66.85	31.21	26.96	39.96
AU20	284.30	290.71	22.84	789.05	104.62	70.07	19.33	15.12	54.38
AU21	358.10	104.67	37.88	838.13	60.88	48.67	21.13	28.71	59.19
AU22	339.79	230.92	14.63	486.67	125.38	79.85	28.88	16.69	43.03
AU23	292.35	375.35	9.81	528.71	59.64	51.95	33.62	25.09	40.89
AU24	245.65	214.08	43.80	575.85	52.57	55.07	12.04	26.59	54.07
SE25	267.25	343.21	33.10	372.62	132.82	58.12	20.85	12.58	42.44
SE26	205.71	185.63	38.24	654.06	36.62	61.93	9.67	10.04	49.03
SE27	246.62	171.22	11.49	263.87	85.08	55.93	15.29	29.63	37.06
SE28	271.32	279.28	22.74	505.74	108.80	66.16	18.72	20.93	45.48
SE29	380.66	238.10	18.39	594.51	117.24	61.04	31.98	11.97	40.86
SE30	387.43	240.40	35.36	519.48	145.67	41.06	11.24	12.82	47.14
OC31	248.93	183.86	31.10	348.47	27.88	50.84	30.62	27.77	42.60
OC32	231.68	394.07	13.20	157.80	90.82	68.38	28.26	29.16	30.00
OC33	345.22	124.40	24.56	362.41	156.04	58.61	35.90	13.35	37.79
OC34	238.60	303.79	15.22	501.02	63.71	41.90	13.12	16.66	33.83
OC35	308.78	299.61	28.50	444.61	40.45	67.71	37.98	28.00	33.53
OC36	368.00	223.46	9.86	300.90	92.37	75.12	12.14	13.47	34.00
NO37	350.72	225.59	12.70	158.21	110.48	64.10	43.49	27.58	27.61
NO38	308.60	231.89	12.25	174.86	111.10	53.75	14.81	28.99	29.89

NO39	269.28	362.35	21.35	392.41	115.52	42.87	31.51	19.26	30.07
NO40	351.12	313.24	9.79	338.46	101.47	56.95	43.54	28.42	25.09
NO41	248.66	263.90	26.96	294.73	83.05	73.06	9.45	22.15	37.45
NO42	319.67	275.43	12.24	201.41	79.28	42.38	25.89	26.83	30.61
DE43	317.33	225.20	17.14	296.20	87.27	46.85	26.02	26.29	34.97
DE44	368.38	111.76	4.55	175.25	65.57	42.48	41.26	22.60	22.73
DE45	351.20	157.15	16.06	396.87	51.63	72.73	9.13	28.93	27.22
DE46	377.33	114.93	16.90	542.49	148.67	49.88	13.21	27.20	35.95
DE47	316.77	107.36	15.20	347.49	41.18	75.96	27.56	28.62	24.91
DE48	316.40	298.80	28.83	340.90	89.22	76.11	13.61	26.68	33.92
JA49	302.97	219.40	7.69	311.49	95.74	64.94	16.66	25.19	24.80
JA50	280.50	280.62	26.41	257.39	112.48	52.40	29.45	23.36	35.21
JA51	325.37	109.63	15.06	234.58	91.75	78.89	28.96	11.41	28.96
JA52	384.78	355.39	12.13	289.09	184.31	72.06	18.08	21.45	25.27
JA53	207.36	200.64	17.72	206.99	68.84	63.83	5.60	16.57	31.65
JA54	368.84	294.10	14.30	143.27	113.60	43.29	16.97	14.67	24.66
FE55	302.67	234.03	8.42	415.01	123.49	46.41	9.99	11.45	26.30
FE56	339.32	259.17	23.13	174.12	93.99	68.79	26.81	15.77	31.26
FE57	201.76	120.29	29.67	520.51	75.46	55.16	5.25	15.31	34.91
FE58	347.88	187.04	15.17	389.61	61.23	50.27	23.66	16.38	28.09
FE59	207.94	370.39	15.67	191.47	51.15	48.29	19.55	25.77	34.07
FE60	240.78	322.20	19.74	436.21	54.66	65.74	6.50	10.18	32.36
MR61	347.52	397.76	15.20	321.56	104.95	45.90	35.45	27.03	32.35
MR62	291.67	337.60	32.25	327.24	77.29	69.39	20.71	14.66	39.81
MR63	381.30	364.53	18.36	443.44	102.19	68.82	15.25	22.70	39.07
MR64	219.13	287.53	7.62	413.33	59.60	79.30	8.77	12.78	26.26
MR65	360.54	297.88	6.42	376.36	112.13	77.50	25.96	16.01	26.73
MR66	279.86	229.72	19.48	373.61	130.13	78.53	7.56	16.37	32.46
AP67	367.92	128.25	27.04	506.43	122.15	58.09	13.98	14.66	35.12
AP68	354.00	346.62	13.63	339.51	169.21	65.79	44.25	17.06	31.70
AP69	255.17	228.99	8.82	367.57	35.72	65.68	26.28	29.99	25.94
AP70	242.80	141.65	21.68	232.05	83.04	63.74	6.80	15.10	25.50
AP71	231.18	158.22	24.65	392.87	76.52	45.51	13.87	21.30	39.13
AP72	369.20	195.76	13.41	192.08	94.52	50.04	30.27	11.67	23.95
64-90 microns									
MA1	399.06	172.09	8.21	427.09	135.28	64.49	28.31	26.38	22.90
MA2	373.09	371.62	16.10	446.98	95.35	64.10	43.32	10.39	25.86
MA3	379.75	359.31	15.23	303.04	105.10	32.77	28.73	26.30	19.83
MA4	473.05	497.56	7.25	214.54	180.95	30.94	16.11	18.14	16.82
MA5	298.82	221.23	12.98	256.73	42.94	53.50	29.98	10.26	15.61
MA6	419.21	240.80	8.03	204.39	187.97	40.97	50.74	19.43	20.01
JN7	248.46	449.02	17.90	434.39	113.09	54.08	10.71	21.23	26.62
JN8	516.12	414.90	5.23	290.33	222.70	42.40	45.75	20.34	22.63
JN9	459.51	337.73	4.85	135.11	201.10	33.54	29.41	19.38	14.90
JN10	282.82	371.39	9.51	132.00	153.53	46.39	27.06	14.99	15.50
JN11	284.04	477.50	13.16	469.74	117.12	58.68	27.03	19.02	20.88
JN12	509.76	155.70	11.17	175.52	85.93	63.45	37.36	30.36	13.08
JU13	270.54	226.41	4.70	183.15	125.54	53.54	32.20	21.24	26.46

JU14	468.86	325.51	20.30	218.09	184.86	38.44	26.58	20.12	34.68
JU15	501.92	460.51	7.98	258.88	143.16	52.86	43.97	26.53	22.63
JU16	445.67	502.07	8.93	464.07	156.77	53.16	23.69	11.85	23.95
JU17	366.89	261.70	25.98	682.15	177.45	48.27	49.39	25.27	31.21
JU18	352.72	205.01	14.93	271.40	152.06	30.65	13.89	17.40	27.24
AU19	369.91	320.85	10.81	258.22	167.13	80.22	40.26	26.42	26.37
AU20	395.18	377.92	14.16	576.01	131.82	79.88	25.91	9.22	38.07
AU21	440.46	132.93	28.41	720.79	82.79	57.92	27.68	24.12	40.84
AU22	438.33	279.41	10.24	515.87	175.54	91.83	35.53	17.69	29.69
AU23	403.44	454.17	6.67	634.45	75.74	46.76	41.35	18.06	25.76
AU24	316.89	297.57	31.53	656.46	72.55	48.46	16.13	16.49	37.85
SE25	334.06	473.63	23.50	339.09	164.70	47.66	27.72	8.55	25.89
SE26	275.65	245.03	24.86	758.71	46.50	47.07	12.47	6.63	37.75
SE27	325.54	229.43	8.16	187.35	114.86	49.22	18.96	26.67	26.31
SE28	355.43	340.72	14.55	525.97	134.91	62.85	26.21	20.09	30.02
SE29	483.44	295.24	14.16	511.28	153.59	64.09	42.85	8.38	29.83
SE30	530.78	305.31	22.63	607.79	182.09	26.28	14.61	13.97	31.58
OC31	331.08	239.02	21.15	271.81	34.01	59.48	41.95	29.44	31.10
OC32	322.04	476.82	8.98	178.31	122.61	71.12	38.72	25.37	22.80
OC33	459.14	155.50	17.69	286.30	212.21	48.06	44.88	8.01	22.67
OC34	288.71	407.08	9.74	320.65	80.27	28.07	16.14	13.99	21.99
OC35	398.33	410.47	18.53	475.73	51.78	61.62	46.34	30.80	21.12
OC36	474.72	268.15	7.79	261.78	111.77	87.14	15.06	11.58	24.48
NO37	448.92	304.55	9.27	131.31	139.20	42.95	54.36	27.58	17.67
NO38	376.49	317.69	9.56	178.35	138.87	58.05	19.70	20.29	21.82
NO39	376.99	471.06	14.09	235.45	150.18	47.16	42.53	11.75	19.85
NO40	449.43	379.02	6.95	240.31	128.87	35.31	60.95	23.59	15.05
NO41	320.77	353.63	19.68	191.58	112.12	47.49	12.57	17.94	28.46
NO42	402.78	344.29	8.45	197.39	95.13	46.19	34.18	26.56	22.04
DE43	409.36	308.52	12.17	319.89	122.17	29.05	36.17	20.51	23.43
DE44	442.06	144.17	2.77	168.24	88.52	50.13	55.29	16.72	14.55
DE45	463.58	193.29	11.88	456.40	71.76	73.46	11.14	30.67	19.33
DE46	528.26	143.66	11.32	640.13	184.35	50.38	16.51	30.19	25.88
DE47	380.12	137.42	9.88	246.72	52.30	90.39	33.90	26.90	16.94
DE48	386.01	367.52	19.03	330.67	110.64	75.35	16.46	29.61	21.03
JA49	396.89	307.16	5.23	246.08	130.20	68.19	22.33	21.92	19.59
JA50	342.21	345.16	16.64	234.22	150.72	42.97	35.93	25.23	26.76
JA51	442.50	148.00	9.34	192.35	115.61	85.99	37.36	9.36	17.67
JA52	500.21	476.22	8.49	338.23	223.01	56.21	23.15	14.59	17.94
JA53	265.42	272.87	14.00	248.39	85.37	44.04	7.28	11.27	23.74
JA54	468.43	382.33	8.58	94.56	146.55	45.89	23.24	13.50	19.23
FE55	399.52	327.64	5.89	273.91	165.48	37.13	12.09	7.79	21.04
FE56	427.54	360.25	14.57	198.49	122.19	58.47	32.70	12.30	24.07
FE57	248.16	155.17	18.10	530.92	93.57	44.68	7.24	13.93	26.18
FE58	469.64	245.02	11.07	405.19	80.21	55.80	33.12	17.04	17.13
FE59	268.24	503.73	9.87	120.63	68.55	32.84	25.41	21.65	25.55
FE60	310.61	389.86	13.82	296.62	72.15	47.33	7.93	11.61	23.62
MR61	476.10	548.91	9.58	292.62	125.94	39.47	43.95	23.79	25.56

MR62	396.67	425.38	22.25	376.32	102.80	46.49	27.13	9.53	27.47
MR63	472.81	510.34	12.67	465.62	137.95	55.06	19.22	18.39	27.35
MR64	291.44	368.04	4.57	413.33	83.44	91.20	12.18	9.59	18.91
MR65	443.46	366.39	3.85	278.51	144.65	49.60	32.71	16.49	20.58
MR66	358.22	321.61	13.83	317.57	179.59	91.88	10.58	18.50	21.10
AP67	441.50	159.03	17.31	516.56	162.46	44.15	16.92	11.73	23.18
AP68	488.52	464.47	8.86	315.74	223.36	53.95	55.76	18.94	21.87
AP69	334.27	320.59	7.06	301.41	48.23	44.01	35.48	34.79	19.20
AP70	330.21	192.64	14.31	259.90	112.93	59.92	9.52	11.93	15.81
AP71	300.53	202.52	17.75	239.65	91.82	32.77	18.73	21.30	28.56
AP72	443.04	244.70	10.46	197.84	122.87	57.55	40.87	8.75	16.05
90-180 microns									
MA1	530.75	216.83	5.25	491.16	166.40	76.74	35.38	24.53	13.74
MA2	492.48	460.81	10.63	478.27	121.10	72.43	53.28	6.23	18.88
MA3	508.86	485.07	10.97	269.71	129.27	33.75	39.07	17.09	15.07
MA4	662.27	611.99	4.64	182.36	228.00	30.94	19.65	21.58	12.11
MA5	391.46	307.51	8.69	164.30	54.10	57.25	36.28	9.75	11.87
MA6	557.56	301.01	5.46	210.52	231.20	36.46	65.46	21.57	15.81
JN7	308.09	606.18	12.17	516.93	139.10	39.48	14.77	23.99	20.76
JN8	634.83	526.93	3.19	299.04	302.87	43.25	56.74	16.48	16.30
JN9	565.20	439.05	3.64	132.41	249.36	29.18	39.41	22.87	10.28
JN10	347.86	467.95	7.51	129.36	208.80	35.72	36.53	17.69	10.69
JN11	377.77	649.40	10.00	516.71	159.28	44.01	37.57	19.97	16.50
JN12	693.27	214.87	8.26	150.94	111.71	62.82	47.82	32.49	9.94
JU13	357.11	312.45	3.01	168.50	163.21	34.80	43.47	17.20	20.90
JU14	562.63	419.91	14.01	222.45	258.81	36.52	35.62	17.10	24.28
JU15	682.62	580.25	4.79	209.69	200.42	59.20	55.84	21.76	16.07
JU16	566.00	697.87	7.14	436.23	203.79	45.72	32.45	9.00	18.92
JU17	454.94	345.45	18.19	422.93	227.14	29.93	65.20	29.82	23.41
JU18	426.79	252.17	10.15	214.41	197.68	34.63	18.47	18.44	17.98
AU19	499.37	417.10	7.68	165.26	230.65	58.56	49.12	27.48	20.57
AU20	490.02	457.29	11.19	357.13	170.05	63.11	33.68	10.51	28.17
AU21	541.77	170.15	19.04	627.09	109.29	52.70	35.98	22.91	32.67
AU22	525.99	343.68	7.17	335.32	228.20	60.61	49.74	11.50	18.71
AU23	528.51	563.18	4.07	602.73	98.46	55.64	57.48	20.77	17.00
AU24	418.29	404.70	24.91	466.09	89.23	54.28	20.48	14.67	28.01
SE25	461.01	573.09	17.16	301.79	197.64	32.41	36.87	8.21	17.86
SE26	374.89	338.14	18.89	553.86	60.92	49.89	16.34	6.36	25.29
SE27	426.46	309.74	5.79	192.97	157.36	40.36	24.65	19.73	20.52
SE28	444.29	425.90	10.77	520.71	184.83	50.91	35.91	18.08	21.01
SE29	642.97	383.82	8.92	388.57	205.81	44.22	58.27	6.37	19.39
SE30	695.32	403.01	14.48	607.79	245.82	26.80	19.86	11.18	20.21
OC31	407.22	317.89	16.71	236.47	42.86	44.61	57.89	28.26	24.88
OC32	428.31	610.34	6.28	137.30	158.16	80.36	54.21	16.49	16.64
OC33	606.07	211.48	13.26	209.00	284.37	52.39	55.20	8.57	17.69
OC34	381.09	565.84	6.14	282.18	109.97	26.67	21.47	16.37	14.51
OC35	517.82	525.40	13.34	371.07	62.65	46.21	58.38	20.33	12.67
OC36	645.62	332.51	5.61	264.40	139.71	89.75	19.58	8.46	18.36

NO37	561.15	374.59	7.32	124.74	178.18	49.39	70.67	31.44	13.96
NO38	474.38	441.59	7.17	131.98	169.42	69.08	27.38	18.67	16.58
NO39	467.47	569.98	10.00	155.40	208.75	34.42	59.55	7.28	13.10
NO40	588.76	488.94	4.86	192.25	157.22	27.89	76.19	17.93	9.03
NO41	407.38	438.50	12.79	178.17	142.39	43.69	17.22	16.51	22.20
NO42	515.56	471.67	5.66	157.91	125.58	33.72	45.80	19.66	15.65
DE43	499.41	413.42	8.76	220.73	153.94	21.79	46.30	19.48	17.57
DE44	579.09	198.96	2.19	136.27	112.42	44.11	75.19	11.54	10.62
DE45	635.11	268.68	8.20	506.60	86.11	71.25	14.26	33.12	14.69
DE46	655.04	176.70	8.15	716.95	252.56	55.42	22.45	20.83	17.60
DE47	494.16	191.01	7.31	278.79	62.76	63.27	41.69	16.41	11.01
DE48	486.37	455.73	15.03	271.15	141.62	70.83	22.06	17.77	14.93
JA49	515.96	371.66	3.19	226.39	177.08	47.73	30.59	20.38	12.54
JA50	468.83	469.42	12.14	271.70	201.97	50.27	44.20	15.14	16.86
JA51	575.25	189.44	6.54	221.21	156.07	76.53	45.95	9.64	13.78
JA52	640.27	666.71	5.69	209.71	287.69	57.33	28.24	11.81	11.84
JA53	323.81	373.83	9.38	149.03	116.95	37.00	8.81	12.51	17.09
JA54	590.22	458.80	5.41	112.53	186.12	50.02	29.75	12.69	14.23
FE55	555.34	458.70	3.65	304.04	203.54	33.79	16.68	4.98	13.47
FE56	517.33	453.91	10.64	168.72	171.06	50.87	41.86	12.18	18.05
FE57	317.65	209.49	11.58	472.52	123.51	35.30	9.63	14.21	20.95
FE58	563.57	318.53	7.42	352.52	106.68	51.34	44.38	14.48	10.28
FE59	337.99	604.48	6.42	78.41	82.94	25.28	31.51	20.78	18.14
FE60	422.42	495.12	10.36	234.33	87.30	32.66	9.68	8.36	15.35
MR61	571.32	735.54	5.75	330.66	152.39	25.26	54.94	18.32	19.93
MR62	531.54	540.23	15.35	361.27	130.55	46.96	33.91	7.91	20.33
MR63	638.30	658.34	10.14	284.03	189.00	34.69	26.33	13.61	20.51
MR64	361.39	485.81	2.74	409.20	106.81	77.52	16.45	8.63	11.34
MR65	580.94	487.30	2.62	206.09	186.59	46.62	43.83	12.86	13.79
MR66	501.51	398.79	11.06	244.53	226.28	90.04	14.07	17.02	12.66
AP67	600.45	200.38	11.08	309.94	227.44	30.02	21.32	8.68	16.23
AP68	615.54	575.94	6.82	353.63	290.37	41.54	76.94	12.50	14.00
AP69	424.53	445.61	4.66	247.15	63.66	50.17	46.13	36.18	14.78
AP70	455.69	233.10	10.01	280.69	141.16	50.93	12.56	9.19	9.49
AP71	387.69	253.15	14.02	179.74	122.13	29.82	25.65	20.87	22.85
AP72	567.09	303.43	7.95	201.80	167.10	37.98	49.45	6.39	10.91
180-250 microns									
MA1	700.59	281.88	4.04	574.65	199.68	67.53	46.00	16.44	10.44
MA2	669.77	557.58	6.48	478.27	147.74	52.15	70.33	5.98	14.91
MA3	641.17	674.24	6.91	178.01	179.68	32.40	50.79	20.34	9.95
MA4	880.82	777.23	3.43	167.77	291.84	35.27	26.73	22.45	7.27
MA5	528.47	384.39	6.43	139.66	74.66	68.12	48.97	6.82	8.66
MA6	735.97	400.34	3.28	181.05	291.31	23.33	81.17	17.26	9.48
JN7	415.92	745.60	8.89	387.69	168.31	26.45	18.91	20.63	12.66
JN8	876.06	732.43	2.55	311.00	387.67	31.57	72.62	13.51	12.55
JN9	700.84	540.03	2.40	146.97	326.66	34.14	51.63	19.90	6.78
JN10	473.09	650.45	5.18	146.17	288.15	40.72	47.12	10.97	8.45
JN11	521.32	896.17	7.60	428.87	211.84	34.33	49.22	19.37	10.06

JN12	873.53	275.03	5.78	172.08	135.16	67.22	60.25	27.61	5.96
JU13	499.96	381.19	2.14	178.61	228.49	28.19	56.95	16.17	16.10
JU14	782.06	558.48	10.23	251.37	310.57	35.79	43.10	12.31	14.81
JU15	942.01	800.74	3.73	132.11	244.52	71.05	78.18	17.62	10.77
JU16	730.14	907.24	4.78	318.44	258.82	28.34	39.91	6.57	14.00
JU17	564.13	466.35	12.73	317.20	297.55	28.13	82.80	33.39	16.62
JU18	512.14	350.51	6.39	229.42	253.03	32.55	22.72	16.96	14.03
AU19	639.20	575.60	5.60	152.04	279.08	43.92	61.40	28.03	15.84
AU20	597.82	571.61	8.73	428.55	224.47	38.49	41.09	9.78	20.84
AU21	698.88	214.39	12.75	727.42	135.52	49.02	50.01	21.08	23.52
AU22	662.75	436.47	4.52	331.96	310.35	54.55	68.63	7.59	11.60
AU23	739.91	749.02	2.52	548.48	125.05	51.74	75.87	18.90	11.56
AU24	522.87	530.15	18.93	419.48	116.00	58.62	26.42	9.83	16.80
SE25	585.48	739.29	12.87	229.36	251.00	25.28	46.83	5.67	10.90
SE26	461.11	463.26	13.22	382.16	79.19	53.38	22.87	7.57	15.43
SE27	579.98	433.63	4.29	171.74	201.42	46.82	32.54	22.50	14.57
SE28	577.57	545.15	7.97	416.57	234.73	49.38	45.24	17.00	14.50
SE29	855.15	518.15	6.24	345.83	284.02	52.18	73.42	7.13	14.73
SE30	973.45	536.00	10.14	522.70	314.66	17.96	24.04	9.17	12.73
OC31	553.83	419.62	12.03	182.08	54.00	48.63	76.99	21.19	15.42
OC32	578.21	750.71	3.96	163.39	216.68	67.50	71.02	10.72	11.48
OC33	775.77	285.50	8.09	248.71	349.77	62.86	71.76	6.43	12.73
OC34	495.42	684.67	4.60	251.14	131.96	30.94	30.06	18.17	8.71
OC35	709.42	688.27	10.54	241.20	76.43	43.44	75.90	22.77	9.76
OC36	903.87	422.29	3.76	264.40	174.63	86.16	27.02	7.02	13.95
NO37	690.22	475.73	4.39	84.83	219.16	34.57	96.82	25.78	8.65
NO38	583.49	569.65	5.16	87.11	216.86	67.01	36.97	15.31	11.44
NO39	598.36	723.87	7.10	93.24	258.85	37.52	79.20	7.72	8.91
NO40	724.17	601.39	3.31	123.04	205.96	20.64	92.96	19.00	6.50
NO41	521.45	526.20	7.80	158.57	192.23	30.58	24.10	18.65	15.76
NO42	623.83	641.48	3.62	132.64	165.76	26.98	63.66	16.90	10.64
DE43	689.19	549.85	5.78	161.13	212.43	20.91	56.94	16.95	12.30
DE44	793.36	244.71	1.36	88.58	143.90	28.23	94.74	13.39	7.33
DE45	762.13	338.54	5.33	430.61	114.53	53.44	18.25	22.85	9.25
DE46	903.96	242.09	5.05	458.85	340.95	56.53	28.29	18.12	10.74
DE47	662.18	252.14	5.41	228.61	80.33	70.87	54.62	13.78	8.15
DE48	637.14	551.43	10.37	211.50	177.02	55.95	27.35	19.37	9.41
JA49	624.31	516.61	2.01	172.06	239.06	53.94	40.07	21.81	8.02
JA50	562.59	600.86	9.23	304.30	250.44	30.16	53.48	9.08	13.15
JA51	805.36	259.53	4.90	212.36	201.34	45.92	62.03	10.50	9.51
JA52	857.97	893.39	3.41	236.97	365.36	43.00	34.74	10.28	7.46
JA53	408.00	489.72	6.00	99.85	163.73	26.64	11.36	12.13	10.25
JA54	755.48	568.91	3.51	68.64	256.84	34.01	40.46	15.22	9.39
FE55	760.81	637.59	2.81	285.80	268.67	33.45	21.68	5.28	9.83
FE56	719.08	562.85	7.55	109.67	232.65	36.63	55.67	11.20	14.44
FE57	416.12	261.86	9.04	567.02	149.45	36.36	13.29	11.94	16.76
FE58	676.28	414.09	5.12	415.97	148.28	40.04	61.24	17.38	8.22
FE59	469.80	803.95	4.24	59.59	100.36	18.96	42.85	18.70	11.43

FE60	570.27	643.66	6.22	260.11	104.76	25.47	12.19	7.94	10.59
MR61	748.43	948.84	4.43	314.13	190.49	23.75	75.82	17.58	12.16
MR62	738.84	745.51	12.28	390.17	165.80	53.06	42.39	7.36	16.06
MR63	785.10	803.18	7.60	337.99	257.04	32.60	34.23	15.10	15.59
MR64	491.49	626.70	1.95	450.12	146.33	86.04	22.20	7.25	8.85
MR65	708.74	657.86	1.96	131.90	240.70	48.96	56.54	15.18	10.34
MR66	631.90	482.54	7.52	163.84	307.74	63.03	17.45	16.85	10.00
AP67	756.56	242.46	7.20	322.33	279.75	33.62	26.64	7.38	9.90
AP68	830.97	714.17	4.30	360.70	371.67	49.02	96.18	10.37	10.78
AP69	568.87	543.65	3.63	190.31	82.12	49.66	64.58	43.42	9.46
AP70	555.94	314.68	7.31	232.97	194.81	53.98	16.21	8.63	5.69
AP71	472.98	316.44	11.22	116.83	170.98	18.49	31.04	23.38	16.22
AP72	748.56	421.76	5.57	228.03	213.89	32.66	66.27	4.47	8.18

0-63 microns				
Sample	**Sulphate**	**Nitrate**	**Chloride**	**% Organics**
MA1	354.97	10.97	35.09	31.20
MA2	293.86	14.03	44.30	36.39
MA3	362.49	7.16	39.52	41.88
MA4	413.88	11.83	37.35	36.51
MA5	495.39	9.70	43.99	26.72
MA6	395.21	11.97	42.17	31.31
JN7	327.72	6.10	44.85	42.64
JN8	375.82	5.25	42.55	35.21
JN9	313.16	14.92	44.59	38.86
JN10	478.23	5.20	49.31	28.03
JN11	562.96	10.29	43.32	43.25
JN12	582.60	7.76	40.32	32.08
JU13	253.85	18.67	38.05	42.94
JU14	469.08	10.67	46.87	31.26
JU15	541.49	28.40	36.77	26.56
JU16	204.56	31.70	35.01	34.90
JU17	477.94	26.77	47.55	34.89
JU18	305.85	21.03	35.69	38.20
AU19	270.66	11.80	43.79	36.84
AU20	499.63	21.27	37.93	43.00
AU21	368.98	12.21	48.10	32.97
AU22	322.10	15.00	44.07	28.19
AU23	286.93	23.09	36.20	42.65
AU24	403.52	26.02	46.91	37.78
SE25	247.93	8.02	44.83	37.79
SE26	246.76	13.55	42.64	26.67
SE27	233.95	11.30	47.71	43.23
SE28	337.04	7.06	48.55	26.50
SE29	387.43	7.85	36.75	44.95
SE30	460.37	12.28	46.17	30.67
OC31	471.67	13.86	44.37	26.78
OC32	225.85	13.11	40.80	38.89

OC33	252.72	14.40	40.98	42.22
OC34	229.14	8.31	45.58	31.23
OC35	482.16	8.03	46.19	35.94
OC36	468.96	9.74	37.87	30.46
NO37	238.47	7.48	49.76	43.47
NO38	317.23	6.68	42.98	31.59
NO39	526.83	5.20	37.47	26.56
NO40	536.03	10.77	43.62	35.67
NO41	444.94	8.88	46.57	34.80
NO42	293.26	14.20	43.53	32.21
DE43	500.89	13.39	244.09	44.39
DE44	379.51	6.60	281.46	37.65
DE45	396.78	10.51	246.89	35.55
DE46	463.32	6.06	155.88	36.69
DE47	502.47	9.18	155.74	44.95
DE48	294.03	7.58	165.37	28.74
JA49	243.80	8.29	202.75	38.70
JA50	226.60	13.79	215.06	39.59
JA51	236.91	14.46	206.36	32.08
JA52	397.02	7.23	235.68	36.74
JA53	459.74	5.12	188.28	39.97
JA54	451.18	12.16	281.28	30.79
FE55	405.99	13.14	270.22	28.52
FE56	214.29	5.52	255.66	43.69
FE57	214.92	7.49	223.41	25.03
FE58	508.30	10.86	241.13	39.41
FE59	218.96	8.12	238.84	36.38
FE60	208.45	10.90	219.39	31.44
MR61	515.80	12.40	165.89	39.36
MR62	539.01	11.77	163.11	32.28
MR63	557.46	9.02	121.29	37.52
MR64	265.65	11.42	138.22	31.25
MR65	457.19	6.15	133.58	33.31
MR66	338.76	9.74	121.41	37.15
AP67	466.86	12.70	99.85	35.37
AP68	522.15	12.99	96.64	43.44
AP69	222.21	12.70	83.41	25.12
AP70	486.59	7.69	85.95	27.03
AP71	502.51	7.53	58.02	30.66
AP72	541.19	14.53	112.56	29.29
64-90 microns				
MA1	92.29	12.07	45.97	8.11
MA2	49.96	11.93	62.02	10.19
MA3	43.50	8.52	55.33	24.71
MA4	74.50	10.06	53.78	17.89
MA5	69.35	8.92	63.35	14.43
MA6	118.56	10.89	57.35	18.16
JN7	91.76	6.28	62.79	12.79

JN8	108.99	5.57	56.17	13.73
JN9	50.11	14.92	53.95	23.32
JN10	105.21	4.58	72.49	12.33
JN11	95.70	9.47	53.28	12.98
JN12	174.78	6.44	57.25	12.51
JU13	48.23	20.54	52.89	10.31
JU14	70.36	9.07	60.46	18.13
JU15	113.71	31.81	54.05	7.97
JU16	45.00	36.46	54.97	15.71
JU17	124.26	28.64	71.33	15.35
JU18	85.64	20.40	43.54	19.10
AU19	70.37	14.16	58.68	10.32
AU20	74.94	22.97	45.90	17.20
AU21	110.69	13.55	73.59	16.49
AU22	86.97	18.00	70.51	14.94
AU23	48.78	23.32	51.40	17.06
AU24	121.06	23.16	59.11	8.69
SE25	69.42	7.06	63.66	12.47
SE26	61.69	15.85	58.42	6.13
SE27	30.41	11.64	69.18	25.94
SE28	33.70	6.28	77.68	6.36
SE29	104.61	7.85	47.78	22.03
SE30	64.45	12.28	67.87	7.36
OC31	108.48	14.69	59.90	16.07
OC32	24.84	13.90	55.49	12.83
OC33	42.96	13.25	54.09	23.64
OC34	29.79	7.48	61.08	9.68
OC35	62.68	7.87	72.52	14.74
OC36	70.34	7.89	60.21	6.70
NO37	28.62	6.36	73.64	11.74
NO38	57.10	5.88	67.05	12.64
NO39	84.29	4.21	56.58	5.84
NO40	117.93	11.42	59.32	12.84
NO41	129.03	9.06	64.27	20.18
NO42	82.11	16.61	64.86	11.60
DE43	65.12	15.26	351.49	11.10
DE44	64.52	7.19	422.19	11.67
DE45	63.48	11.77	323.43	18.13
DE46	97.30	6.12	191.73	13.94
DE47	90.44	10.56	210.25	14.38
DE48	32.34	8.57	253.02	6.90
JA49	36.57	8.21	291.96	14.32
JA50	47.59	16.13	273.13	20.98
JA51	42.64	11.57	323.99	16.36
JA52	75.43	6.07	377.09	12.49
JA53	87.35	5.73	288.07	18.39
JA54	117.31	10.09	413.48	13.55
FE55	52.78	12.75	421.54	14.55

FE56	53.57	5.74	370.71	24.90
FE57	36.54	8.91	312.77	14.02
FE58	71.16	12.05	330.35	8.67
FE59	30.65	6.58	296.16	16.73
FE60	31.27	8.72	307.15	14.46
MR61	77.37	11.16	265.42	11.02
MR62	75.46	13.06	239.77	18.72
MR63	83.62	7.76	188.00	8.25
MR64	69.07	11.19	183.83	16.88
MR65	59.43	5.47	191.02	12.32
MR66	91.47	9.45	146.91	9.29
AP67	121.38	12.83	157.76	8.84
AP68	88.77	12.73	117.90	11.29
AP69	42.22	11.81	129.29	12.31
AP70	87.59	9.15	104.86	8.65
AP71	110.55	8.96	76.59	10.42
AP72	140.71	12.64	148.58	10.54
90-180 microns				
MA1	88.60	12.19	39.99	7.46
MA2	58.45	14.31	64.50	12.02
MA3	46.54	9.12	61.41	24.22
MA4	81.95	9.55	63.47	19.68
MA5	57.56	9.28	68.41	12.12
MA6	130.42	10.67	65.95	17.07
JN7	105.53	5.97	66.56	14.20
JN8	98.09	5.62	64.03	14.69
JN9	40.59	16.86	57.73	27.51
JN10	93.64	5.35	60.16	13.94
JN11	110.06	10.32	60.21	10.90
JN12	199.25	6.57	63.55	10.01
JU13	51.61	20.95	59.77	9.89
JU14	77.40	9.98	63.49	14.50
JU15	101.20	31.49	48.11	7.01
JU16	46.80	33.54	45.62	17.12
JU17	135.45	25.49	70.61	18.42
JU18	76.22	16.93	37.45	19.86
AU19	64.04	12.74	48.12	10.62
AU20	79.44	20.67	39.93	16.68
AU21	88.56	15.86	83.16	14.67
AU22	86.10	20.88	76.15	14.49
AU23	57.56	20.99	47.29	17.23
AU24	105.32	21.07	51.42	8.95
SE25	70.81	5.93	73.21	11.72
SE26	70.94	17.76	57.25	6.32
SE27	28.89	13.97	78.86	26.20
SE28	27.97	7.54	73.80	5.91
SE29	115.07	7.69	46.82	20.48
SE30	66.39	11.67	57.69	6.99

OC31	99.81	13.52	60.50	19.12
OC32	27.82	16.68	59.37	14.12
OC33	43.82	12.45	51.93	27.66
OC34	24.72	6.28	60.47	11.33
OC35	63.31	7.55	73.24	15.03
OC36	62.61	7.42	71.05	6.17
NO37	32.91	5.21	80.27	12.79
NO38	50.82	6.00	68.39	13.90
NO39	81.76	4.21	62.80	5.55
NO40	136.79	11.30	56.36	12.71
NO41	138.06	9.42	71.98	24.22
NO42	65.69	16.12	65.51	12.76
DE43	61.21	16.94	407.73	8.88
DE44	76.13	5.90	485.52	12.61
DE45	63.48	11.65	294.32	19.76
DE46	79.78	6.73	210.91	11.71
DE47	101.30	10.13	243.89	12.51
DE48	27.17	9.59	237.84	7.04
JA49	35.47	6.89	251.09	17.18
JA50	40.45	13.23	237.62	24.97
JA51	35.39	9.25	330.46	15.38
JA52	89.77	5.41	331.84	11.62
JA53	76.87	5.45	325.52	16.73
JA54	98.54	9.89	425.89	15.04
FE55	63.33	12.49	425.76	15.56
FE56	51.97	5.51	418.90	28.89
FE57	35.81	7.13	294.01	11.21
FE58	77.57	13.86	379.90	10.14
FE59	36.48	5.85	310.97	14.56
FE60	26.89	7.76	304.07	14.03
MR61	80.46	13.17	246.84	9.70
MR62	90.55	15.29	213.40	16.48
MR63	89.47	6.75	154.16	8.83
MR64	61.47	13.09	189.35	19.58
MR65	47.55	4.82	192.93	12.32
MR66	74.09	8.60	168.94	10.96
AP67	115.31	12.83	183.01	7.34
AP68	73.68	13.62	106.11	10.16
AP69	43.49	10.04	142.21	11.08
AP70	84.08	7.78	111.15	8.74
AP71	109.45	7.62	67.40	12.51
AP72	166.04	14.79	129.26	11.60
180-250 microns				
MA1	77.08	10.36	44.79	7.84
MA2	47.93	11.45	61.92	9.62
MA3	39.56	7.66	71.24	23.00
MA4	80.31	11.08	62.83	20.66
MA5	65.05	10.21	68.41	13.45

MA6	155.20	8.54	60.02	14.17
JN7	126.63	6.03	79.20	12.07
JN8	114.76	6.58	63.39	15.43
JN9	35.31	19.22	53.11	28.61
JN10	96.45	5.84	69.19	15.05
JN11	128.77	11.97	65.63	11.66
JN12	161.39	5.32	63.55	9.61
JU13	42.83	21.58	65.74	8.41
JU14	91.33	10.18	57.14	12.91
JU15	89.06	36.84	57.73	6.24
JU16	51.02	32.53	48.36	17.46
JU17	109.71	30.59	69.20	17.32
JU18	80.03	18.12	38.57	19.07
AU19	67.24	10.45	39.94	12.32
AU20	72.29	18.19	32.34	17.85
AU21	86.78	15.70	94.80	16.43
AU22	78.35	23.18	70.06	13.19
AU23	55.83	24.77	42.56	14.13
AU24	99.00	17.70	43.20	7.97
SE25	67.98	5.57	81.99	11.72
SE26	84.42	18.29	48.66	6.32
SE27	33.23	14.67	74.92	24.89
SE28	26.30	8.90	64.94	5.21
SE29	125.42	7.54	40.26	18.85
SE30	59.75	9.57	51.92	6.85
OC31	112.78	12.43	56.87	16.25
OC32	33.39	17.01	56.40	15.67
OC33	47.33	11.33	46.22	27.66
OC34	21.51	7.35	67.72	9.97
OC35	68.37	8.23	83.50	15.48
OC36	55.09	8.68	78.87	5.12
NO37	33.24	5.16	94.72	10.36
NO38	53.36	5.82	74.54	11.95
NO39	96.48	4.00	63.43	5.61
NO40	134.06	10.51	53.54	15.26
NO41	146.35	9.70	77.02	27.37
NO42	69.63	14.99	74.02	11.61
DE43	50.80	16.60	448.50	9.23
DE44	74.61	4.72	402.98	11.72
DE45	66.02	12.70	314.92	17.19
DE46	93.35	6.73	217.23	12.18
DE47	109.40	8.61	236.57	10.76
DE48	32.60	8.06	249.73	6.40
JA49	34.41	6.76	231.00	17.53
JA50	43.68	11.25	201.98	21.72
JA51	35.04	7.87	270.98	14.92
JA52	96.05	4.38	378.29	9.64
JA53	87.63	4.90	289.71	19.41

JA54	100.51	11.77	489.77	14.59
FE55	60.80	13.12	506.65	13.70
FE56	44.17	6.12	414.71	33.22
FE57	42.97	6.63	235.21	13.23
FE58	74.46	11.51	353.31	11.46
FE59	36.11	6.79	276.76	13.69
FE60	26.08	8.46	355.77	16.69
MR61	94.14	14.09	251.78	8.83
MR62	108.66	17.88	251.81	19.44
MR63	106.47	7.83	143.37	7.24
MR64	73.77	11.00	181.77	16.64
MR65	38.04	3.90	167.85	10.48
MR66	84.46	8.60	143.60	9.64
AP67	137.22	12.06	153.72	6.83
AP68	58.94	16.21	97.62	11.69
AP69	44.79	8.63	150.75	9.19
AP70	85.76	9.26	114.49	8.82
AP71	108.35	8.53	72.79	11.88
AP72	152.75	13.75	125.39	9.98

Appendix 5

Indoor dust chemical analysis

The results for Building One are displayed. The data for all the buildings can be supplied if requested.

0-63 microns									
	Al	**Ca**	**Cu**	**Fe**	**K**	**Mg**	**Mn**	**Pb**	**Zn**
May	125.66	168.09	5.80	129.24	57.01	37.64	15.53	12.10	15.31
June	121.41	314.17	8.37	115.22	70.77	27.41	14.98	13.19	16.74
July	170.01	365.42	9.51	183.12	47.59	22.71	16.38	10.38	25.32
August	168.86	360.29	12.35	368.06	40.18	33.52	10.72	15.54	29.15
September	137.79	279.42	14.07	300.73	48.01	26.39	8.08	9.96	24.45
October	168.32	267.61	9.39	215.05	52.62	36.26	12.38	12.84	14.12
November	187.89	317.76	8.10	156.01	44.07	24.43	13.21	12.00	18.07
December	174.03	214.88	10.69	220.41	32.24	35.19	8.94	10.69	12.88
January	196.33	352.78	9.80	117.83	57.78	26.90	12.54	8.82	19.61
February	114.82	360.84	8.57	170.15	32.96	32.35	6.42	9.80	19.63
March	200.54	411.73	7.12	169.17	51.79	32.86	13.07	12.60	18.36
April	191.13	279.88	10.92	196.28	58.12	38.37	9.26	10.61	13.60
64-90 microns									
May	365.77	230.19	8.26	293.01	161.79	54.41	38.50	20.36	23.30
June	372.71	400.07	10.37	290.58	137.00	47.37	26.12	20.32	17.31
July	419.15	307.42	12.00	337.63	150.22	39.41	33.90	19.85	24.87
August	354.24	293.09	17.58	548.53	108.07	67.04	27.28	19.28	31.08
September	422.95	336.94	17.98	517.18	113.26	51.90	23.57	15.00	30.32
October	384.69	284.42	13.85	285.94	97.82	60.08	30.70	19.95	24.44
November	418.07	357.36	11.90	172.63	108.29	49.01	40.60	22.99	20.88
December	400.54	228.50	10.04	339.44	95.62	62.26	28.72	24.38	21.57
January	343.83	281.71	10.94	227.67	143.47	59.44	26.18	14.20	18.61
February	324.93	301.88	12.26	265.34	101.96	41.16	17.10	12.79	24.10
March	391.41	434.88	10.85	367.69	126.48	54.19	25.44	15.71	22.72
April	372.92	284.06	13.37	334.48	129.10	53.35	32.79	15.65	21.88
90-180 microns									
May	597.48	248.82	4.73	322.42	181.11	56.15	44.93	21.16	15.32
June	485.88	516.98	8.24	276.35	180.35	46.39	36.98	19.33	14.44
July	463.11	393.39	8.77	305.82	222.06	38.41	38.20	17.51	21.17
August	503.66	391.90	12.07	437.52	140.42	57.02	42.80	16.64	24.94
September	544.53	361.00	13.10	372.45	181.01	38.81	29.97	10.83	17.73
October	427.51	458.43	10.34	264.07	138.93	54.85	46.28	18.00	17.14
November	560.23	460.50	7.79	139.50	150.67	40.58	44.42	16.82	13.38
December	553.73	248.29	8.23	317.44	135.31	46.88	32.18	20.00	15.15
January	521.65	378.21	6.86	212.91	162.50	47.51	30.04	12.11	13.64
February	385.88	361.14	7.26	266.54	118.19	38.09	27.83	13.26	14.74
March	562.68	508.57	8.20	285.46	165.44	50.79	32.82	14.28	15.13
April	524.26	316.16	9.41	245.90	178.76	36.51	35.81	15.04	14.39

180-250 microns									
May	703.20	293.69	3.42	403.92	232.97	49.84	67.53	18.40	10.33
June	594.56	589.40	5.57	253.25	265.11	43.33	52.11	17.27	9.90
July	737.57	509.86	5.89	202.18	273.73	33.38	55.83	17.41	13.97
August	581.79	437.99	8.24	452.48	209.72	44.06	51.48	14.20	16.73
September	734.63	489.64	8.49	361.62	239.79	41.32	38.86	11.42	12.14
October	654.69	526.67	7.74	246.77	152.70	55.91	64.02	13.36	13.20
November	647.28	574.39	5.54	102.48	194.91	36.33	72.51	17.19	10.49
December	679.06	383.46	5.52	281.64	172.67	49.75	49.13	16.85	8.88
January	676.31	618.64	5.23	161.21	258.93	36.41	36.16	12.62	8.58
February	652.64	499.71	5.23	242.84	182.09	27.17	32.69	12.85	10.62
March	682.03	632.59	6.09	267.92	202.32	48.11	41.35	14.70	11.07
April	562.54	414.46	6.15	213.32	216.02	40.64	50.50	15.84	9.69

0-63 microns				
	Sulphate	Nitrate	Chloride	% Organics
May	333.8301	5.0468	25.1095	33.7554
June	316.8588	4.2092	26.4940	46.2147
July	326.6517	12.3516	17.9955	43.8375
August	276.1502	11.3036	21.4167	49.8218
September	302.9677	5.7057	27.9983	38.4652
October	255.6600	7.8692	24.7264	46.5845
November	302.4509	3.5473	19.7948	45.2865
December	384.7783	4.7988	122.8606	42.5544
January	288.8525	5.7998	106.3528	54.4675
February	271.5395	4.1089	161.7659	41.9164
March	325.3209	5.7475	88.5675	39.3624
April	397.5190	4.9969	50.0668	42.9548
64-90 microns				
May	114.7052	10.2285	45.8220	13.6876
June	109.3328	7.4500	65.4325	12.6668
July	82.0140	25.6607	49.5737	14.7298
August	91.7932	21.2668	56.6921	12.9858
September	62.8393	10.4857	64.3530	12.9533
October	60.9820	10.7155	57.5209	12.8144
November	77.7737	9.1101	70.0087	12.0238
December	76.0981	10.9826	296.3974	11.7103
January	69.4427	8.3921	284.6620	15.4702
February	47.6051	9.4811	316.3352	14.3421
March	76.6784	9.8664	172.5234	11.8934
April	107.4044	10.1614	117.3508	11.3267
90-180 microns				
May	93.5215	11.8771	58.7470	11.2608
June	113.4662	8.0937	67.4381	15.7101
July	70.5328	20.8027	50.0555	15.8291
August	78.2441	20.3676	50.5843	14.5746
September	60.4314	11.5330	66.6070	12.4077
October	55.7215	10.6178	69.9150	15.1656

November	73.8823	9.3979	63.3635	14.6659
December	68.5198	9.1435	340.3150	12.5195
January	61.1165	7.8441	307.5565	15.1040
February	45.5097	8.8472	324.3087	14.4584
March	63.6561	10.1104	206.7033	14.3272
April	91.5693	11.6900	136.4946	10.0023
180-250 microns				
May	107.6624	8.8827	46.4829	10.1661
June	121.9388	8.3893	57.0094	15.5286
July	79.0315	21.9260	49.4437	15.0465
August	68.3116	16.6448	46.3900	12.0381
September	68.2997	9.6148	53.3774	11.7268
October	50.2068	10.5471	68.5006	12.8315
November	95.9616	8.7898	64.7173	14.2539
December	76.6791	9.8304	276.1267	12.1151
January	62.0484	7.0770	333.5601	16.4149
February	46.5795	9.5330	322.7892	17.0325
March	90.8293	10.4237	203.7123	12.8276
April	107.6702	11.0648	115.7898	9.2649

Appendix 6

Settled dust chemical analysis

One month of EDX analysis for Building One is displayed as an example. All the results can be supplied if requested.

	Elements (Percentage)																		
Particle No.	**S**	**Na**	**Mg**	**K**	**Cl**	**Ca**	**Si**	**Al**	**Fe**	**Ti**	**Cu**	**Ba**	**Zn**	**P**	**Sl**	**Mn**	**V**	**Pb**	**Sc**
1	2	50	3	1	45	0	-	-	-	-	-	-	-	-	-	-	-	-	-
2	-	-	-	2	-	-	60	37	-	2	-	-	-	-	-	-	-	-	-
3	-	42	-	1	36	4	8	7	3	-	-	-	-	-	-	-	-	-	-
4	-	-	-	2	-	-	60	36	-	2	-	-	-	-	-	-	-	-	-
5	8	46	17	2	21	6	-	-	-	-	-	-	-	-	-	-	-	-	-
6	7	43	24	1	22	3	-	-	-	-	-	-	-	-	-	-	-	-	-
7	-	-	-	-	5	95	-	-	-	-	-	-	-	-	-	-	-	-	-
8	-	-	-	-	-	11	89	-	-	-	-	-	-	-	-	-	-	-	-
9	2	43	4	0	50	1	-	-	-	-	-	-	-	-	-	-	-	-	-
10	2	41	5	1	50	1	-	-	-	-	-	-	-	-	-	-	-	-	-
	S	**Na**	**Mg**	**K**	**Cl**	**Ca**	**Si**	**Al**	**Fe**	**Ti**	**Cu**	**Ba**	**Zn**	**P**	**Sl**	**Mn**	**V**	**Pb**	**Sc**
11	3	28	6	2	18	3	20	10	9	1	-	-	-	-	-	-	-	-	-
12	3	-	-	-	-	-	5	1	84	1	5	-	2	-	-	-	-	-	-
13	3	53	6	1	35	1	-	-	-	-	-	-	-	-	-	-	-	-	-
14	1	54	-	1	43	1	-	-	-	-	-	-	-	-	-	-	-	-	-
15	-	-	-	-	-	T	-	-	-	-	-	-	-	-	-	-	-	-	-
16	1	8	3	1	18	9	40	7	4	2	5	-	3	-	-	-	-	-	-
17	1	57	-	1	41	-	-	-	-	-	-	-	-	-	-	-	-	-	-
18	3	11	-	3	7	50	10	15	2	-	-	-	-	-	-	-	-	-	-
19	-	-	18	-	-	-	34	26	22	-	-	-	-	-	-	-	-	-	-
20	1	19	3	1	18	5	43	7	4	-	-	-	-	-	-	-	-	-	-
	S	**Na**	**Mg**	**K**	**Cl**	**Ca**	**Si**	**Al**	**Fe**	**Ti**	**Cu**	**Ba**	**Zn**	**P**	**Sl**	**Mn**	**V**	**Pb**	**Sc**
21	-	-	-	-	0	98	2	-	-	-	-	-	-	-	-	-	-	-	-
22	-	-	-	-	-	98	2	-	-	-	-	-	-	-	-	-	-	-	-
23	1	51	5	1	40	1	-	-	-	-	-	-	-	-	-	-	-	-	-
24	18	27	-	3	24	24	4	-	-	-	-	-	-	-	-	-	-	-	-
25	1	-	-	-	-	0	5	-	89	-	4	-	-	-	-	-	-	-	-
26	1	16	-	1	7	7	50	15	3	-	-	-	-	-	-	-	-	-	-
27	2	-	-	-	1	96	2	-	-	-	-	-	-	-	-	-	-	-	-
28	2	56	5	0	35	1	-	-	-	-	-	-	-	-	-	-	-	-	-
29	2	28	3	1	35	7	12	6	5	1	-	-	-	-	-	-	-	-	-
30	2	28	2	1	35	5	14	7	4	1	-	-	-	-	-	-	-	-	-
	S	**Na**	**Mg**	**K**	**Cl**	**Ca**	**Si**	**Al**	**Fe**	**Ti**	**Cu**	**Ba**	**Zn**	**P**	**Sl**	**Mn**	**V**	**Pb**	**Sc**
31	-	49	-	-	51	-	-	-	-	-	-	-	-	-	-	-	-	-	-
32	1	-	-	17	4	5	54	14	4	-	-	-	-	-	-	-	-	-	-
33	1	52	4	-	43	-	-	-	-	-	-	-	-	-	-	-	-	-	-

34	1	51	9	1	37	1	-	-	-	-	-	-	-	-	-	-	-	-	-
35	6	58	-	-	34	-	1	-	-	-	-	-	-	-	-	-	-	-	-
36	-	46	-	1	37	5	8	4		-	-	-	-	-	-	-	-	-	-
37	-	-	-	-	-	-	T	-	-	-	-	-	-	-	-	-	-	-	-
38	-	46	-	-	54	-	-	-	-	-	-	-	-	-	-	-	-	-	-
39	-	51	5	-	44	1	-	-	-	-	-	-	-	-	-	-	-	-	-
40	-	46	-	-	54	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	S	**Na**	**Mg**	**K**	**Cl**	**Ca**	**Si**	**Al**	**Fe**	**Ti**	**Cu**	**Ba**	**Zn**	**P**	**Sl**	**Mn**	**V**	**Pb**	**Sc**
41	6	58	-	-	34	-	1	-	-	-	-	-	-	-	-	-	-	-	-
42	-	14	-	-	8	73	4	1	-	-	-	-	-	-	-	-	-	-	-
43	0	50	8	1	40	1	-	-	-	-	-	-	-	-	-	-	-	-	-
44	0	-	0	1	64	10	15	4	4	-	-	-	-	-	-	-	-	-	-
45	1	33	3	2	31	8	12	4	5	1	-	-	-	-	-	-	-	-	-
46	0	49	5	1	45	0	-	-	-	-	-	-	-	-	-	-	-	-	-
47	4	64	-	-	31	-	-	-	-	-	-	-	-	-	-	-	-	-	-
48	-	-	-	-	-	93	7	-	-	-	-	-	-	-	-	-	-	-	-
49	1	52	7	1	39	1	-	-		-	-	-	-	-	-	-	-	-	-
50	4	64	-	-	32	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	S	**Na**	**Mg**	**K**	**Cl**	**Ca**	**Si**	**Al**	**Fe**	**Ti**	**Cu**	**Ba**	**Zn**	**P**	**Sl**	**Mn**	**V**	**Pb**	**Sc**
51	2	50	3	1	43	2	-	-	-	-	-	-	-	-	-	-	-	-	-
52	-	-	-	2	-	-	60	37	-	2	-	-	-	-	-	-	-	-	-
53	-	42	-	1	36	4	8	7	3	-	-	-	-	-	-	-	-	-	-
54	-	-	-	2	-	-	60	36	-	2	-	-	-	-	-	-	-	-	-
55	8	46	17	2	21	6	-	-	-	-	-	-	-	-	-	-	-	-	-
56	7	43	24	1	22	3	-	-	-	-	-	-	-	-	-	-	-	-	-
57	-	-	-	-	5	95	-	-	-	-	-	-	-	-	-	-	-	-	-
58	-	-	-	-	-	11	89	-	-	-	-	-	-	-	-	-	-	-	-
59	2	43	4	0	50	1	-	-	-	-	-	-	-	-	-	-	-	-	-
60	2	41	5	1	50	1	-	-	-	-	-	-	-	-	-	-	-	-	-
	S	**Na**	**Mg**	**K**	**Cl**	**Ca**	**Si**	**Al**	**Fe**	**Ti**	**Cu**	**Ba**	**Zn**	**P**	**Sl**	**Mn**	**V**	**Pb**	**Sc**
61	3	28	6	2	18	3	20	10	9	1	-	-	-	-	-	-	-	-	-
62	3	-	-	-	-	-	5	1	84	1	5	-	2	-	-	-	-	-	-
63	3	53	7	1	35	1	-	-	-	-	-	-	-	-	-	-	-	-	-
64	1	54	-	1	43	1	-	-	-	-	-	-	-	-	-	-	-	-	-
65	-	-	-	-	-	T	-	-	-	-	-	-	-	-	-	-	-	-	-
66	1	8	3	1	18	10	40	7	4	2	5	-	3	-	-	-	-	-	-
67	1	57	-	1	42	-	-	-	-	-	-	-	-	-	-	-	-	-	-
68	3	11	-	3	7	50	10	15	2	-	-	-	-	-	-	-	-	-	-
69	-	-	18	-	-	-	34	26	22	-	-	-	-	-	-	-	-	-	-
70	1	19	3	1	18	4	43	7	4	-	-	-	-	-	-	-	-	-	-
	S	**Na**	**Mg**	**K**	**Cl**	**Ca**	**Si**	**Al**	**Fe**	**Ti**	**Cu**	**Ba**	**Zn**	**P**	**Sl**	**Mn**	**V**	**Pb**	**Sc**
71	-	-	-	-	0	98	2	-	-	-	-	-	-	-	-	-	-	-	-
72	-	-	-	-	-	98	2	-	-	-	-	-	-	-	-	-	-	-	-
73	2	51	5	1	40	1	-	-	-	-	-	-	-	-	-	-	-	-	-
74	18	27	-	3	24	24	4	-	-	-	-	-	-	-	-	-	-	-	-
75	1	-	-	-	-	0	5	-	89	-	4	-	-	-	-	-	-	-	-
76	1	16	-	1	7	7	50	15	2	-	-	-	-	-	-	-	-	-	-
77	2	-	-	-	1	96	2	-	-	-	-	-	-	-	-	-	-	-	-

78	2	56	5	0	35	2	-	-	-	-	-	-	-	-	-	-	-	-	-
79	2	28	2	1	35	7	12	6	5	0	-	-	-	-	-	-	-	-	-
80	2	28	2	1	35	6	14	7	4	1	-	-	-	-	-	-	-	-	-
	S	**Na**	**Mg**	**K**	**Cl**	**Ca**	**Si**	**Al**	**Fe**	**Ti**	**Cu**	**Ba**	**Zn**	**P**	**Sl**	**Mn**	**V**	**Pb**	**Sc**
81	-	49	-	-	51	-	-	-	-	-	-	-	-	-	-	-	-	-	-
82	1	-	-	17	4	5	54	14	4	-	-	-	-	-	-	-	-	-	-
83	1	52	4	-	43	-	-	-	-	-	-	-	-	-	-	-	-	-	-
84	1	51	9	1	37	1	-	-	-	-	-	-	-	-	-	-	-	-	-
85	6	58	-	-	34	-	1	-	-	-	-	-	-	-	-	-	-	-	-
86	-	46	-	1	37	5	8	4	0	-	-	-	-	-	-	-	-	-	-
87	-	-	-	-	-	-	T	-	-	-	-	-	-	-	-	-	-	-	-
88	-	46	-	-	54	-	-	-	-	-	-	-	-	-	-	-	-	-	-
89	-	50	5	-	44	1	-	-	-	-	-	-	-	-	-	-	-	-	-
90	-	46	-	-	54	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	S	**Na**	**Mg**	**K**	**Cl**	**Ca**	**Si**	**Al**	**Fe**	**Ti**	**Cu**	**Ba**	**Zn**	**P**	**Sl**	**Mn**	**V**	**Pb**	**Sc**
91	6	58	-	-	34	-	1	-	-	-	-	-	-	-	-	-	-	-	-
92	-	14	-	-	8	73	4	1	-	-	-	-	-	-	-	-	-	-	-
93	0	50	8	1	40	1	-	-	-	-	-	-	-	-	-	-	-	-	-
94	0	-	1	1	64	9	15	4	4	-	-	-	-	-	-	-	-	-	-
95	1	33	3	2	31	8	12	4	5	1	-	-	-	-	-	-	-	-	-
96	-	49	5	1	45	0	-	-	-	-	-	-	-	-	-	-	-	-	-
97	4	64	-	-	32	-	-	-	-	-	-	-	-	-	-	-	-	-	-
98	-	-	-	-	-	93	7	-	-	-	-	-	-	-	-	-	-	-	-
99	1	51	7	1	39	2	-	-	0	-	-	-	-	-	-	-	-	-	-
100	4	64	-	-	32	-	-	-	-	-	-	-	-	-	-	-	-	-	-

Appendix 7

Publications as a result of this research

Peer-reviewed journal articles:

Shilton, V., Giess, P., Mitchell, D. and Williams, C. (2002). The characterisation of settled dust by scanning electron microscopy and energy dispersive X-Ray analysis. *Water, Air and Soil pollution: Focus*. 2 (5-6). pp. 237-246.

Shilton, V., Giess, P., Mitchell, D. and Williams, C. (2002). The relationships between indoor and outdoor respirable particulate matter: meteorology, chemistry and personal exposure. *Indoor and Built Environment*. 11 (5). pp. 266-274.

Conference contributions:

Shilton, V. F., Giess, P., Mitchel, D., and Williams, C. (2001). Characterisation of settled dust by scanning electron microscopy and energy dispersive x-ray analysis. The Third International Conference on Urban Air Quality, 19-23rd of March 2001, Loutraki, Greece.

Shilton, V. F. (2002). The indoor and outdoor relationships of respirable particulate matter. Science, Engineering and Technology for Britain, 18th of March 2002, London, UK.

Shilton, V F., Giess, P., Mitchell, M. and Williams, C. (2002). The relationships between indoor and outdoor respirable particulate matter: meteorology, chemistry and personal exposure, 11-12th of April 2002, Lancaster University, UK.

Published in proceedings:

Shilton, V., Giess, P., Mitchell, D. and Williams, C. (2001) The characterisation of settled dust by SEM and EDX analysis. Proceedings of the fifth international conference on urban air quality and fifth saturn workshop. 19th to 23rd of March 2001, Loutraki, Greece. Extended abstracts CD ROM.

Shilton, V., Giess, P., Mitchell, D. and Williams, C. (2002). The relationships between indoor and outdoor respirable particulates: meteorology, chemistry and personal exposure. Proceedings of the aerosol society 13th annual conference. 11th and 12th of April 2002, Lancaster, UK. pp. 53-56.

Other articles:

Shilton, V. F. (2000). Airborne particulate matter: indoor/outdoor relationships and personal exposure. *The Aerosol Society Newsletter*. 37. pp. 6-8.

Shilton, V. F. (2001). Indoor and outdoor respirable particulate concentrations and chemical composition. *The Aerosol Society Newsletter*. 39. pp. 12-14.

On the proceeding pages are copies of articles published in peer-reviewed journals as an outcome of this research. Other articles have also appeared in non-peer reviewed publications and these can be supplied if requested.

Indoor Built Environment

Original Paper

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The Relationships between Indoor and Outdoor Respirable Particulate Matter: Meteorology, Chemistry and Personal Exposure

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Key Words
Indoor/outdoor ratio · Respirable particulate matter · Meteorology · Street canyon · Particulate chemistry

Abstract
Respirable particulate matter was collected inside and outside of a building located in Wolverhampton city centre during the same time period between 19/9/00 and 1/5/01. A total of 103 pairs of indoor and outdoor measurements were made using Casella personal dust monitors. The building monitored was located in a small street canyon produced by 4- and 5-storey buildings on both sides of the road. The road is the main approach road to a major bus station and is used by large numbers of heavy-duty diesel vehicles each day. The mean concentration for outdoor samples was 27.6 and 9.8 $\mu g \cdot m^{-3}$ for indoor samples. The mean indoor/outdoor ratio for this period was 0.4 (±0.02 SE). Meteorological variables including wind speed, wind direction and precipitation were measured at a nearby urban monitoring station. A greater wind speed caused an increase in the quantity of outdoor generated particulates penetrating indoors. Wind direction affected both indoor and outdoor particulate concentrations, with lower concentrations being observed when the wind direction was parallel to the street canyon. The indoor/outdoor ratio also showed a decrease during parallel wind conditions. During days with high amounts of precipitation, the concentration of particulates, both indoors and outdoors, decreased significantly. The personal exposure of a building occupant was measured for 20 working days in conjunction with outdoor and indoor measurements. Personal exposure concentrations were well correlated with indoor concentrations ($r^2 = 0.98$). Forty of the indoor and outdoor particulate samples of dust were chemically analysed for sulphate, nitrate, chloride, zinc, copper, manganese and aluminium to determine any indoor/outdoor relationships of particulate chemistry and any interrelationships between the analytes.

Introduction

Research into the effects of exposure to air pollution has highlighted a wide range of apparent health effects, including respiratory illness, cardiovascular disease and cancer [1–4]. To aid our understanding of this, air quality monitoring stations are now located at a number of sites to provide information on ambient pollutant concentrations to which the population is exposed. This approach assumes that spatial variations in exposures are minimal, and that a single, daily average exposure estimated from

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these monitoring stations can be applied to the population of a city or region as a whole. However, airborne particulate concentrations can vary significantly over a relatively short distance, for example concentrations near to busy roads may be far higher than background concentrations, especially within street canyons where the dispersion of traffic-related pollutants can be restricted. In addition, many people spend the majority of their time indoors, estimated to be approximately 80–90% of their day [5], and previous research has shown that indoor (I) and outdoor (O) particle concentrations can vary widely [6, 7]. It is important to determine how the particle concentration inside a building is affected by changes in outdoor concentrations and how this may relate to the particle levels to which building inhabitants are exposed. From previous studies it is apparent that I/O ratios can alter considerably from one day to the next, even when building conditions (ventilation, window and door use etc.) remain the same [8–10].

As indoor particulate concentrations are often closely dependent upon ambient concentrations, it may be assumed that any process affecting ambient concentrations will lead to a subsequent change in indoor levels. Meteorological factors can influence both the ambient concentration of airborne particulate matter and the ability of particles to penetrate indoors. Therefore, it seems likely that local meteorology plays a key role in determining the relationships between indoor and outdoor particulate concentrations. One of the key meteorological factors affecting ambient concentrations and therefore, potentially indoor concentrations is precipitation. Precipitation, both solid and liquid, rapidly removes particulates from the atmosphere through many individual processes, such as collision with rainfall and nucleation within fog or mist. This effect is often termed precipitation or below-cloud scavenging [11]. However, once the precipitation event is over, wet deposited particulates may become re-suspended into the atmosphere so that concentrations can quickly return to previous levels. Wind speed and wind direction is likely to be important in determining both ambient particulate concentrations and also the penetration of particulates into buildings. In terms of ambient concentrations, wind speed is important in the re-suspension of settled dusts. The effects of wind speed on ambient particulate concentrations have been investigated in Birmingham, England [12]. A positive correlation was observed between wind speed and coarse particulates during the summer. A similar relationship was also seen for the winter months, but upon closer examination of the results it was clear that this was mainly due to high concentrations of re-suspended coarse particulate matter produced during a few high wind speed events. This indicates that re-suspension during the winter months requires a much greater wind speed, likely to be due to the damper ground surface conditions usual of British winters. In comparison, $PM_{2.5}$ demonstrated a strong negative correlation to wind speed during the summer and the winter. This is possibly because the sources of $PM_{2.5}$ are largely anthropogenic, with a high wind speed causing a dilution effect. It is also generally accepted that a high wind speed causes the ingress of external air indoors, which may lead to an increase in externally generated particulates inside a building.

Within street canyons, wind speed and wind direction can play a significant role in the distribution of traffic-related pollutants. For example, pollutant concentrations are often found to be greater on the leeward side compared to the windward side of the canyon [13]. Most researchers also agree that pollutants released within a street canyon become more diluted with a faster wind speed and an inflow wind direction parallel to the street [13–15].

The I/O ratio of particulate concentrations gives an indication as to whether particulate matter is the result of indoor generation or the penetration from outdoors. In this work, ratios are calculated in terms of I/O and it is expected that in the absence of indoor sources, the ratios between I/O mass concentrations will be less than or equal to 1 [16].

Whilst the majority of epidemiological studies hold the view that particle chemistry has little influence on the health effects of particulate matter it seems likely that certain particle species (e.g. sulphurous and carbonaceous particles) will have a greater influence on health than those particles with a chemical composition similar to that of human tissue (e.g. particles mainly composed of sodium chloride). Nevertheless, the chemistry of particulate matter is important for source apportionment and is, therefore, an essential part of any research or control strategy.

The I/O ratios for different chemical species are highly variable, mainly depending on whether the compound or element in question has an indoor or outdoor source. Those chemical species with an indoor source often display an I/O ratio greater than 1.

Particle size is one of the most important factors when considering chemical I/O relationships. This is because fine particles normally penetrate into buildings with greater efficiency than larger, coarser particles. It has been suggested that particles within the PM_{10} size fraction can

penetrate a building with the same efficiency as non-reactive gases [17]. Therefore, those chemical species associated with small particles often have an I/O ratio closer to 1 than those species associated with larger particles.

The I/O ratio for sulphate is often very close to 1, usually in the range of 0.8–0.9 [8, 18]. It is also generally agreed that sulphate is found almost entirely in fine particles and is unlikely to be found in high quantities in particles greater than about 2.5 μm in diameter [19, 20]. In a study of domestic homes it was also found that I/O ratios for sulphate decreased with increasing particle size (0.9 for $PM_{1.1}$ and 0.5 for PM_{10}) [20], suggesting that very fine particles penetrate more efficiently into a building than coarser particles.

The I/O ratios for elemental species are also closely related to particle size. For example, Ca and Fe often have very low I/O ratios as these elements are normally associated with coarse particles. However, elements such as zinc (Zn), bromine (Br) and lead (Pb) can have higher I/O ratios as these elements are often associated with fine particles, with ratios for these elements normally being in the range 0.5–0.6 [20, 21]. A decrease in the I/O ratio with increasing particle size similar to sulphate has been observed for Pb, although the relationship was not as pronounced [20].

In this research particles have been analysed for sulphate, nitrate and chloride and the metals Zn, copper (Cu), manganese (Mn) and aluminium (Al). These compounds and metals were chosen as sulphate, nitrate, chloride, Zn and Cu normally have anthropogenic or 'urban' sources, including vehicle emissions and building weathering, whereas Mn and Al are often considered as having 'natural' sources such as soil re-suspension [22]. Therefore, an understanding of the chemistry of collected particulate matter can contribute to the knowledge of particulate sources [23]. In addition, it has been suggested that Zn may be a potential tracer element for vehicle emissions [24].

Materials and Methods

Site Description

All samples were collected inside and outside of a University of Wolverhampton building located in Wolverhampton city centre. All indoor samples were collected from a room on the ground floor, the size of the room was 3 × 7 × 3 m. There were two wooden framed sash style windows facing directly onto the road immediately outside the building; the size of these windows was 1 m wide and 1.5 m high. Although the windows could be opened they remained closed for the duration of the monitoring. The room is largely unused and very rarely entered. Because of this the generation of particles in this room is negligible. Tobacco smoking is prohibited and there is no cooking in the building. Outdoor samples were collected at ground level, approximately 10 m further along the road from the room where indoor samples were collected. For personal exposure measurements, an individual was chosen who worked inside this building.

The road outside the building is the main approach road for the city's primary bus station. This road is, therefore, used by a large number of heavy-duty diesel vehicles each day. The road is closed to other vehicles except taxis, so the buses contribute almost 100% of the traffic using the road. Traffic is held up by traffic lights at one end of the road regularly causing queues of vehicles with engines idling outside the two buildings. Four- and five-storey buildings on both sides of the road produce a small street canyon effect which may impede the dispersion of traffic-related emissions. Previous work has demonstrated that high concentrations of airborne particulate matter exist both inside and immediately outside this building [25].

Particulate Sampling

All respirable particulate matter samples were collected using Casella personal dust monitors with the flow rate set at 1.9 litres·min^{-1}. At this flow rate the Casella sampler collects respirable size particles, here defined as those particles with an aerodynamic diameter less than 4 μm. The flow rate was set at the beginning of each sampling period and then measured again after sampling. If the flow rate had altered by more than ± 5% then the sample was discarded.

Glass fibre filter papers (Whatman GF/A 37 mm) were used for all particulate collection. PTFE and etched polycarbonate (Nucleopore) filters were also tested, but both of these filters caused a high flow resistance meaning that the flow rate could not be sustained by the pump for the full 24-hour period. Therefore, glass fibre filters were the preferred choice.

Filter papers were stored in a sealed container with silica gel for 24 h before weighing and 24 h after sample collection before reweighing to drive off any adsorbed water. All weighing was carried out on a Toledo MT5 Micro-balance (Mettler) with a readability of 1 μg.

Control filter papers were also stored with the samples to assess any weight changes that were not due to the particulate loading of the filters. Repeated weighing of blank filters on different days gave measurements that were repeatable to within 1 μg, this being less than 2% of a typical aerosol mass of 50–200 μg.

I/O and Personal Exposure Measurements

Each set of indoor and outdoor samples was collected for a period of 24 h from 12.45 p.m., Monday to Friday between 19/9/00 and 1/5/01. Of the 110 sets of indoor and outdoor samples the flow rate varied outside the ± 5% threshold 7 times, giving 103 pairs of indoor and outdoor measurements.

Personal respirable particulate measurements were also taken for 1 non-smoking individual who worked inside the sample building. The sample inlet was at approximate breathing height (shoulder level). Samples were collected for a total of 23 working days with indoor and outdoor measurements recorded during the same time periods. The sampling duration for the indoor, outdoor and personal exposure measurements was 8 h between 9.00 a.m. and 5.00 p.m. This length of time was chosen in order to coincide with the average working day. The subject was asked to keep a diary of activity indicating the length of time spent outdoors and whether they came into contact with any strong source of particulate matter such as tobacco smoke or cooking. The subject came into contact with such sources for extended time periods on 3 of the sample days. These samples were,

therefore, considered unrepresentative and were discarded. Examination of the activity log for the individual showed that on average only 35 min of the 8-hour working day was spent outside the building.

Chemical Analysis of Particulate Matter

Because the collected particles were to be analysed for chemical composition they were stored in a refrigerator after their final weighing to reduce the loss of volatile species. Unavoidable exposure of the filters to room temperature occurred whilst the filter papers were being conditioned for weighing. Of the 103 pairs of samples collected, the first 20 were used for the determination of Al, Cu, Mn and Zn and the following 20 used for the determination of sulphate, nitrate and chloride.

Because glass fibre filter papers can contain high amounts of impurities a washing regime was used to increase the accuracy of chemical analysis before their use for particle collection. The filter papers were first conditioned by soaking in 70% nitric acid for 2 h and then left in a bath of de-ionised water for 24 h. The filter papers were then rinsed in copious amounts of de-ionised water and allowed to dry in a sealed container with silica gel. The filters were then removed from the container and stored in closed Petri dishes until required for use. Analysis of blank filter papers showed that this washing procedure greatly reduced the blank background concentrations of all the elements analysed. Blank anion concentrations were negligible, even for unwashed filter papers. Control experiments showed that washing the filter papers by this method did not decrease particle retention efficiency of the filter material.

Loaded filter papers were closed vessel microwave digested with 8 ml of 95% sulphuric acid, 4 ml of 32% hydrochloric acid and 2 ml of 55% hydrofluoric acid. This was done in stages with increasing microwave power: 250, 400, 650 and back to 250 W for 6 min at each setting.

The samples were then made up to a volume of 25 ml in acid-washed volumetric flasks with de-ionised water. Any remnants of the filter papers that had not been digested were also transferred into the volumetric flask. This solution was shaken vigorously and allowed to settle in a refrigerator for a minimum of 48 h to allow all the particles in the solution to settle. The solution was then decanted and analysed by inductively coupled plasma atomic emission spectrometry.

The filters for anion analysis were extracted into 10 ml of de-ionised water and mechanically agitated to ensure thorough removal of the particulates. To aid dissolution 1 ml of propan-2-ol was added. Concentrations of chloride, sulphate and nitrate ions were determined using a Dionex DX100 ion chromatograph.

Blank values for anionic and elemental species were obtained by analysing unloaded, washed filter papers from the same batch as the filter papers used for sampling.

Meteorological Recording

Wind speed, wind direction and precipitation were recorded at a nearby urban monitoring station approximately 300 m away from the investigation building. All meteorological results were logged every hour and a 24-hour mean calculated, which corresponded to the sampling period for particulate collection. For wind direction, an automatic weather vane was used which records an average wind direction for the preceding hour.

The mean daily precipitation for the sampling period was 4.24 mm, so for the purposes of data interpretation days were classified as either having zero precipitation, low precipitation or high precipitation. Low precipitation included those days with a quantity of precipitation of less than or equal to 4.24 mm. High precipitation was all those days with a quantity of precipitation greater than 4.24 mm.

Wind direction was classified as either being a parallel wind or a cross-wind. The street canyon is orientated in a west-to-east direction. Therefore, wind with a westerly or easterly direction was classified as a parallel wind and those with a northerly or southerly direction as cross-winds.

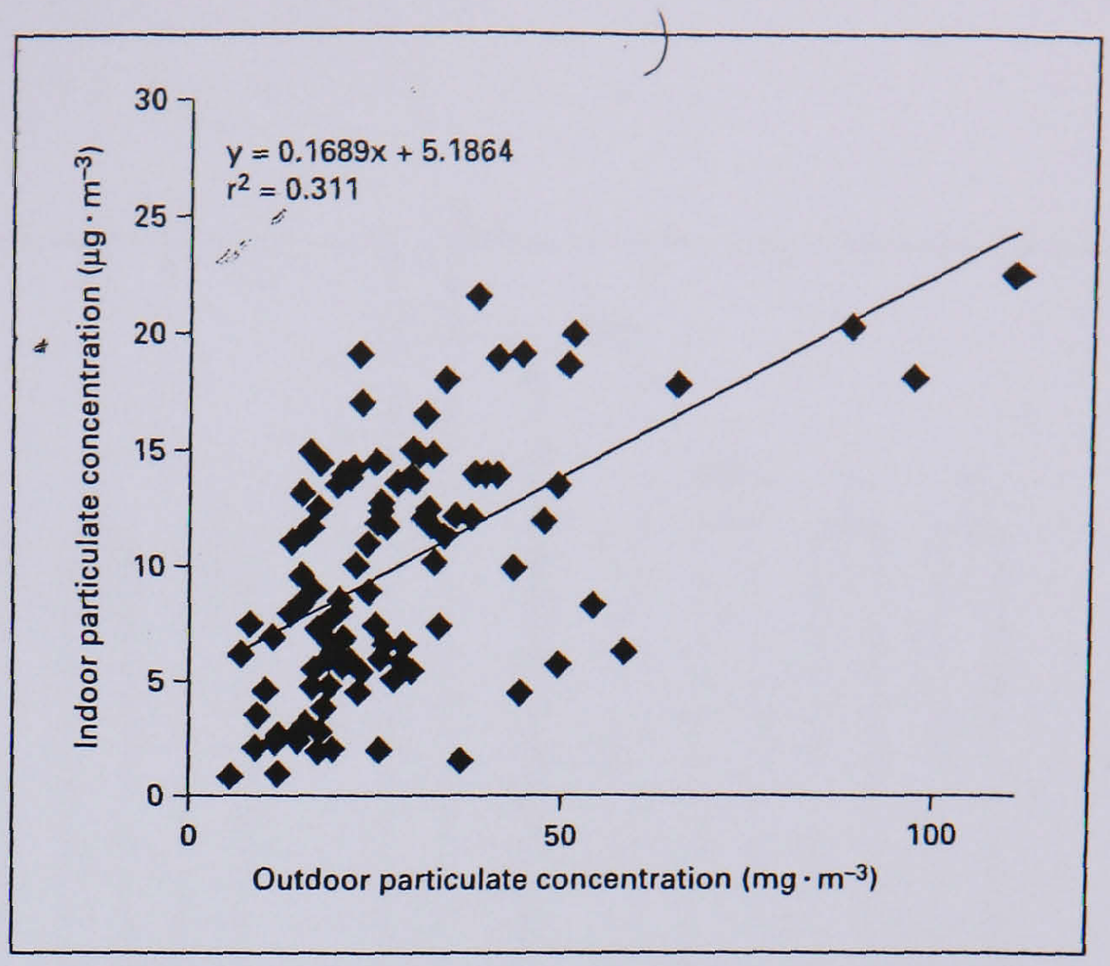


Fig. 1. Regression analysis between indoor respirable particulate concentrations and outdoor respirable particulate concentrations.

Results and Discussion

The mean outdoor and indoor respirable particulate concentrations for the entire sampling period were 27.6 and 9.8 $\mu g \cdot m^{-3}$, respectively, which difference was statistically significant (Student's t test; $p = 0.001$). The mean I/O ratio for the sampling period was 0.4, suggesting an external source of particulate matter. The range of respirable particulate concentrations for indoor and outdoor air was 5–22 and 6–110 $\mu g \cdot m^{-3}$, respectively. The mean I/O ratio recorded here is similar to results for fine particulates measured by other researchers: 0.59 [6] and 0.6 [26]. Indoor and outdoor particulate concentrations are significantly correlated, $r^2 = 0.31$ (fig. 1) ($p = 0.01$). This correlation agrees well with the I/O ratios measured by other researchers, for example, an I/O ratio of 0.34 for PM_{10} [9]. The correlation of 0.31 suggests that in this building indoor concentrations are driven by variations in outdoor concentrations.

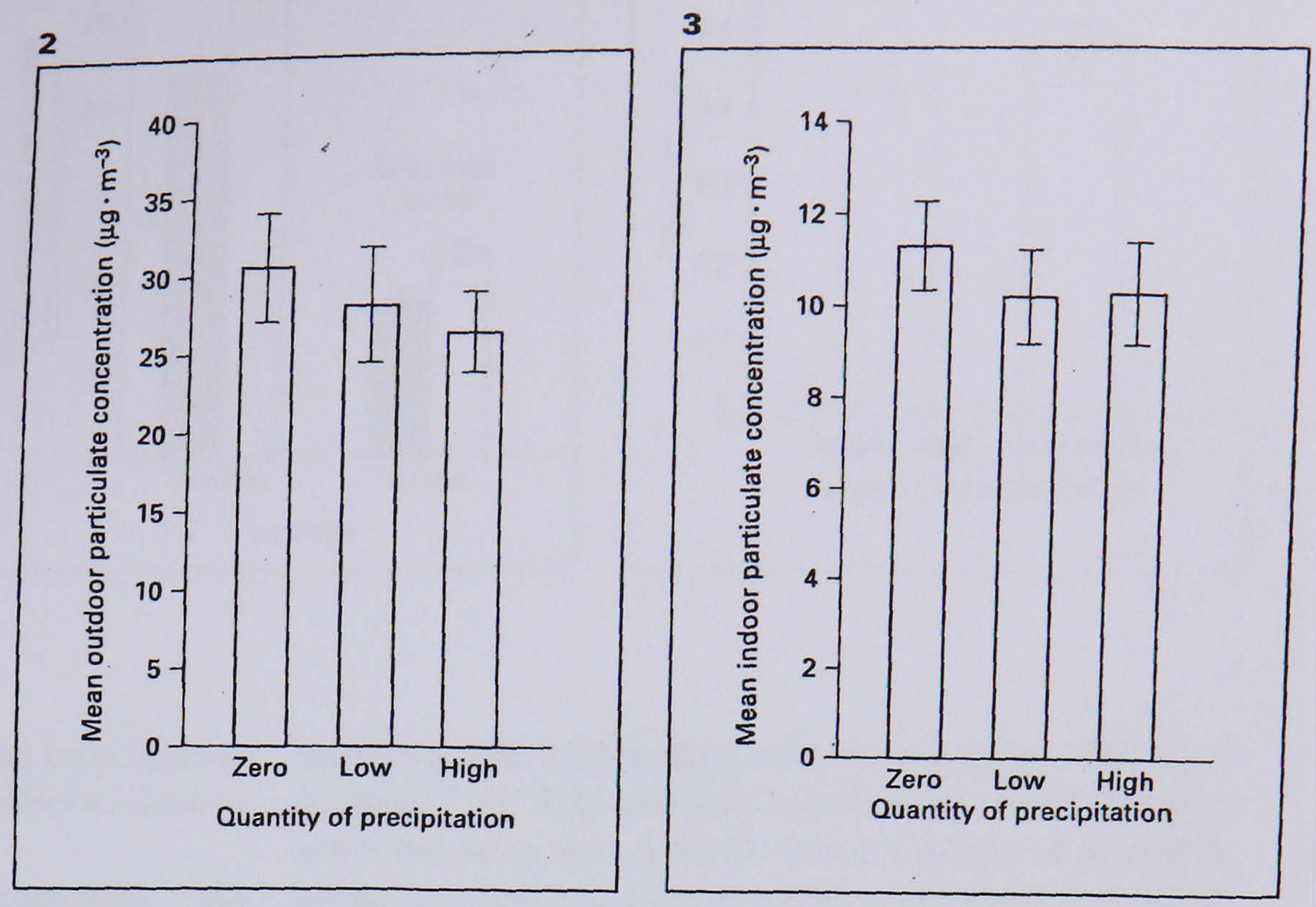


Fig. 2. The effect of precipitation on mean outdoor respirable particulate concentrations.

Fig. 3. The effect of precipitation on mean indoor respirable particulate concentrations.

Precipitation affected both indoor and outdoor particulate concentrations, with days with zero precipitation having the largest mean particulate concentration for both outdoor and indoor samples (fig. 2, 3). ANOVA analysis of both indoor and outdoor results shows the differences in particle concentration between days with zero, low and high rainfall to be statistically significant.($p = 0.05$). Outdoor particulate concentrations were affected more strongly by precipitation. Indoor levels showed a 10% increase between days with high precipitation and those days with zero precipitation, whilst outdoor concentrations increased by almost 16% on days with zero precipitation. A likely explanation for why indoor concentrations are not affected as much as outdoor concentrations is the presence of internally generated particulates. Although there are no obvious sources of indoor particulates inside the room being studied, there may be some internal generation of particulate material elsewhere in the building, which may then be transported into the study room. Particulates generated inside the building will not be removed by a precipitation event.

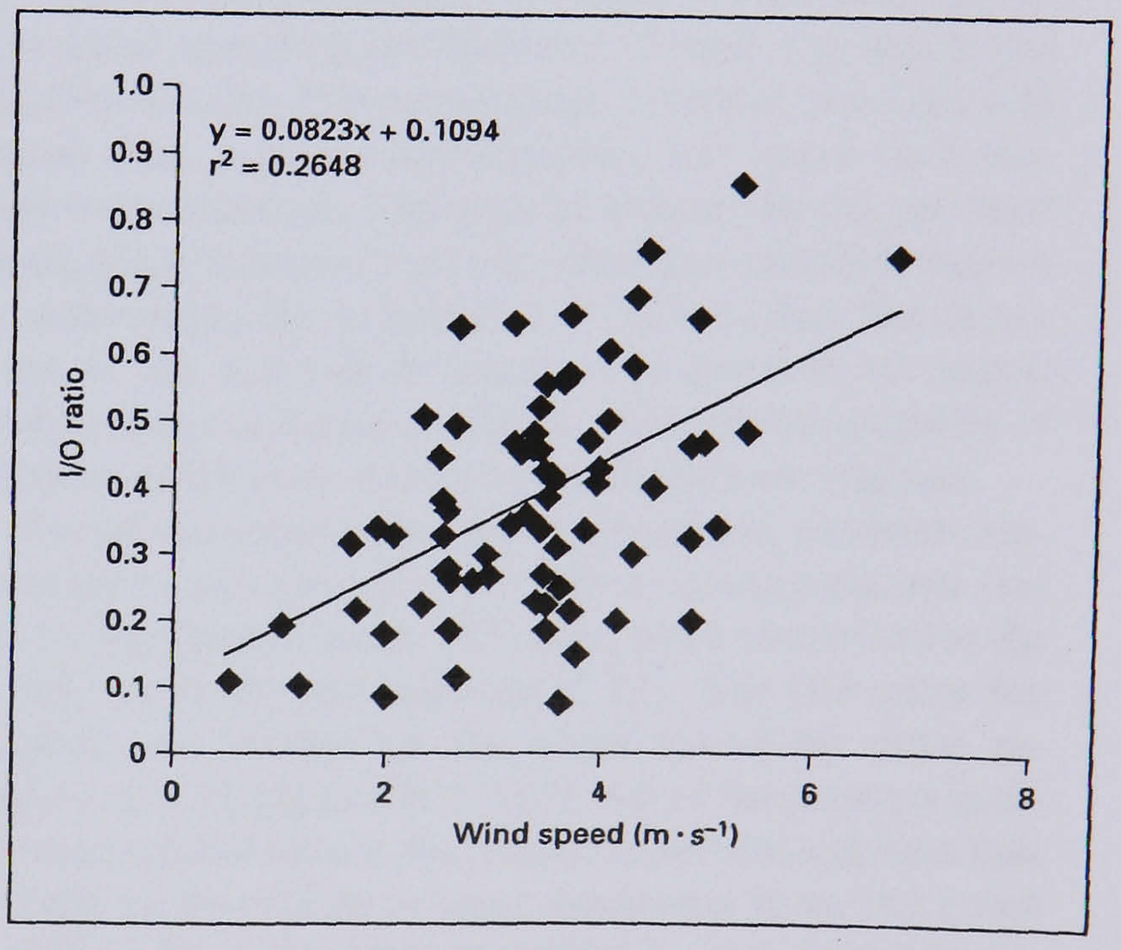
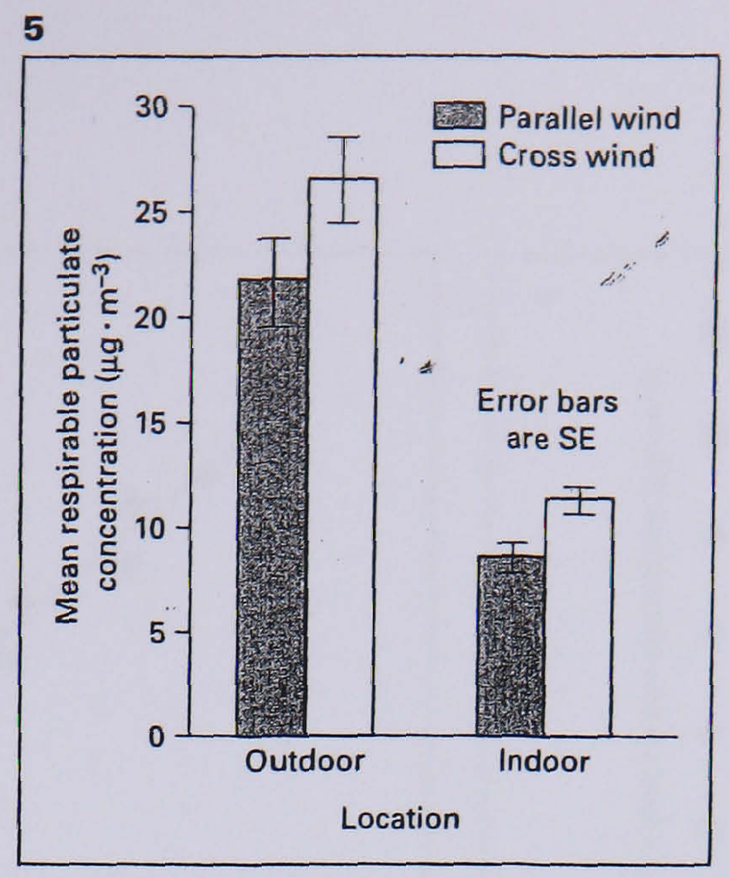


Fig. 4. Regression analysis between wind speed and I/O ratio.

Neither indoor or outdoor respirable particulate concentrations show any discernible relationship to wind speed. Although a significant correlation exists between wind speed and I/O ratio (fig. 4) ($r^2 = 0.26$, $p = 0.02$). It would be expected that an increase in wind speed would lead to a subsequent increase in the penetration of particulates indoors. This is because an increase in wind speed often generates a pressure gradient between indoor and outdoor air, causing ambient air to be drawn into the building. However, increasing wind speed is also often related to an increase in ambient particulate concentrations in open situations and a dilution effect in street canyons. Neither of these relationships are observed here. This is likely to be because the outdoor samples were taken at ground level only, approximately 3 m from the kerb



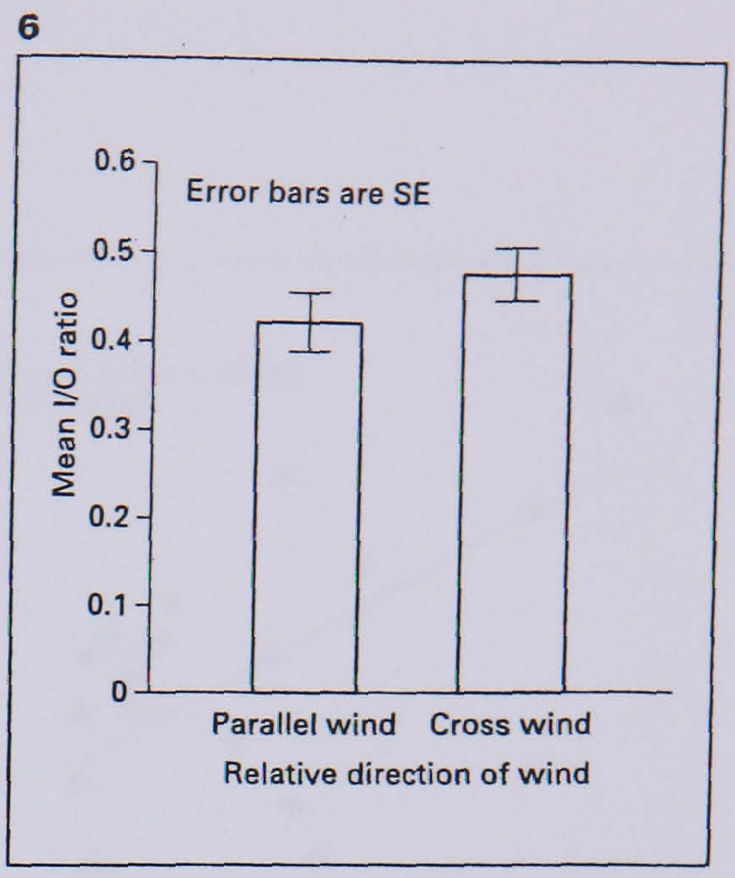


Fig. 5. The effect of wind direction on mean outdoor and mean indoor respirable particulate concentrations.

Fig. 6. The effect of wind direction on mean I/O ratio.

side. Therefore, any dilution effect that may be occurring within the canyon may not be having any effect so close to a strong source of particulate matter.

Wind direction appears to be more important than wind speed, with indoor and outdoor particulate concentrations being closely related to wind direction (fig. 5). Both indoor and outdoor concentrations are lower when the wind direction is parallel to the street canyon. The difference in particulate concentrations for cross-wind and parallel-wind conditions is statistically significant for both indoors and outdoors ($p = 0.05$). This is because cross-wind conditions produce a vortex effect within the canyon, which restricts the dispersion of pollutants causing them to build up to high concentrations, whereas during parallel-wind conditions the air in the canyon will be effectively replaced with cleaner ambient air. The I/O ratio is also greater for cross-wind conditions than for parallel-wind conditions (fig. 6) ($p = 0.05$). This would be expected as wind flowing parallel to the canyon would not cause a significant pressure gradient between indoors and outdoors. However, cross-wind conditions producing vortexes within the canyon may produce pressure gradients between indoor and outdoor air, causing air from outside to be drawn indoors and therefore increasing the I/O ratio. Bernoulli's effect may also be important due to wind speed within the canyon being greater during parallel-wind conditions, producing a lower atmospheric pressure outside the building, causing less external air to be drawn indoors.

A significant correlation is observed between personal exposure and indoor concentrations ($r^2 = 0.989$, $p = 0.001$), but the relationship is less than significant for personal exposure and outdoor concentrations ($r^2 = 0.37$, $p = 0.1$) (fig. 7, 8). The correlation coefficient of 0.37 for personal exposure and outdoor concentrations is generally lower than that recorded by other researchers, for example 0.69 [27]. However, the correlation between personal concentrations and indoor concentrations is stronger than for outdoor concentrations, as might be expected for an individual spending the majority of their day inside the building. During this monitoring, personal exposure was greater than indoor concentrations, but lower than outdoor concentrations. This may be affected by the personal cloud, where a person's activity generates particles around an individual [28]. In addition, it is likely that the movement of the individual causes re-suspension of settled dust on floors and other surfaces, adding to the quantity of airborne particulate matter to which they are exposed.

For all the metals and anions analysed, outdoor concentrations are greater than indoor concentrations (table 1). The largest mean I/O ratios were observed for Zn (0.69), Cu (0.56) and sulphate (0.71). The I/O ratios for sulphate are similar to the ratios found by other researchers: 0.81 [8] and 0.89 [18]. All of these ratios indicate an external source. For zinc, copper and sulphate this is likely to be vehicle exhaust emissions from the buses travelling along the road immediately outside the building. It has been suggested that Zn in combination with Br and antimony could be used as a potential marker elements for motor vehicle emissions, since engine oil contains high concentrations of these elements [24]. However, Zn can also be emitted in large quantities by oil-powered power plants and oil refineries. As there are no oil-powered power plants or oil refineries in the region, it

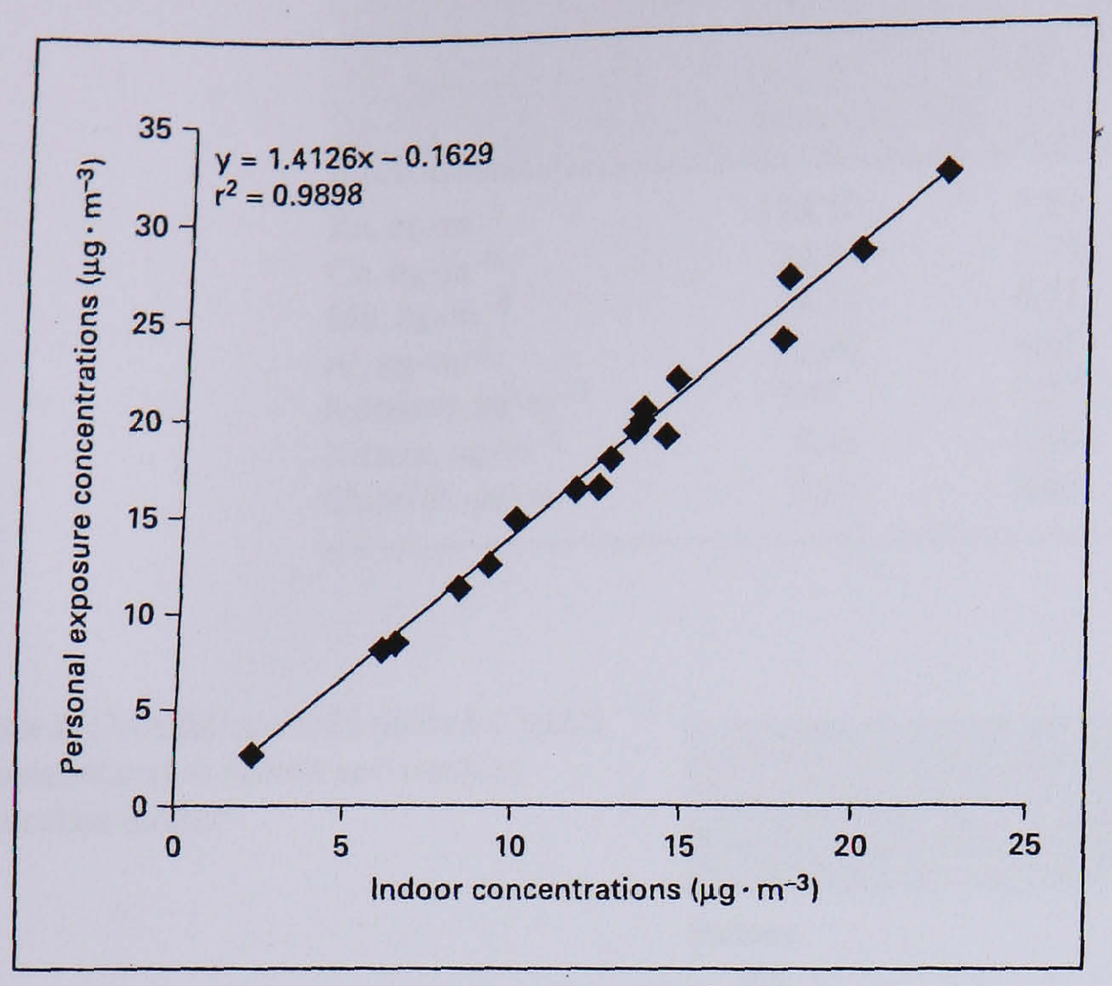


Fig. 7. Regression analysis of indoor respirable particulate concentrations and personal exposure.

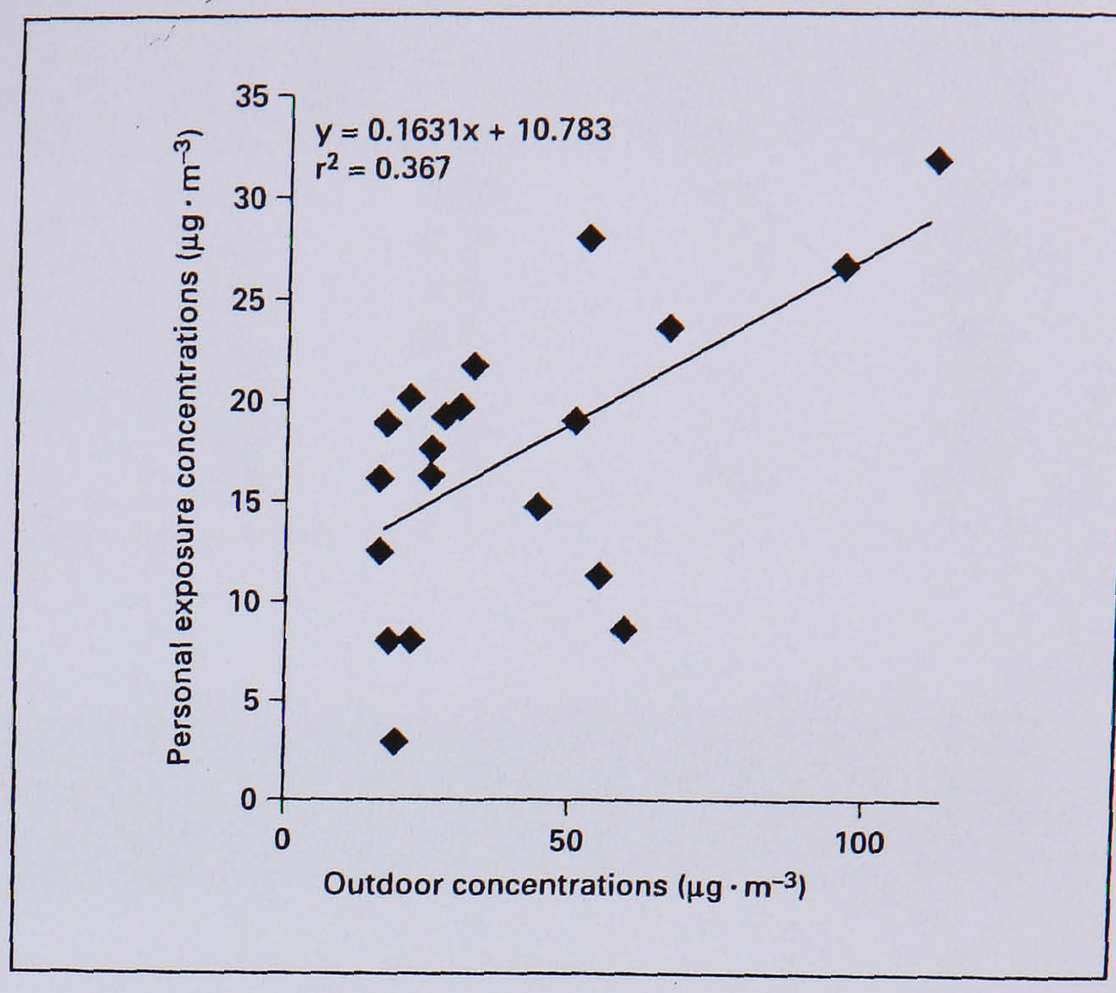


Fig. 8. Regression analysis of outdoor respirable particulate concentrations and personal exposure.

seems likely that the majority of zinc present inside and outside of this building originates from traffic emissions. In addition, there is evidence that Cu can be traced back to motor vehicle emissions [22]. The strong correlation between outdoor Zn and outdoor Cu concentrations (r^2 = 0.742, table 2) suggests that these two elements are indeed originating from the same source, likely to be vehicle emissions. The high I/O ratios for Zn, Cu and sulphate suggest that these particles are efficiently penetrating through the building shell and so are likely to be associated with very fine particles. For example, it has been observed that sulphate is only found above detection limits in particles smaller than 2.1 µm in diameter [20]. Significant correlation coefficients were observed between outdoor and indoor Zn (r^2 = 0.459) and Cu (r^2 = 0.615, table 2). A very strong correlation was also recorded for sulphate (r^2 = 0.93, fig. 9). This is a further indication that Zn, Cu and sulphate are associated with fine particles.

Mean I/O ratios for Mn (0.29), Al (0.18), nitrate (0.37) and chloride (0.11) are lower than for Zn, Cu and sulphate (table 1). This also indicates an external source, but shows that particles of Mn, Al, nitrate and chloride are more efficiently removed by the building shell, so are likely to be associated with coarser particles. This is demonstrated further as I/O relationships for these analytes are not significant (table 2). A likely source of Mn, Al, nitrate and chloride is wind-blown dust and re-suspended street dust [22]. The correlation coefficient between outdoor Mn and outdoor Al (r^2 = 0.551) suggests that these two elements originate from similar sources.

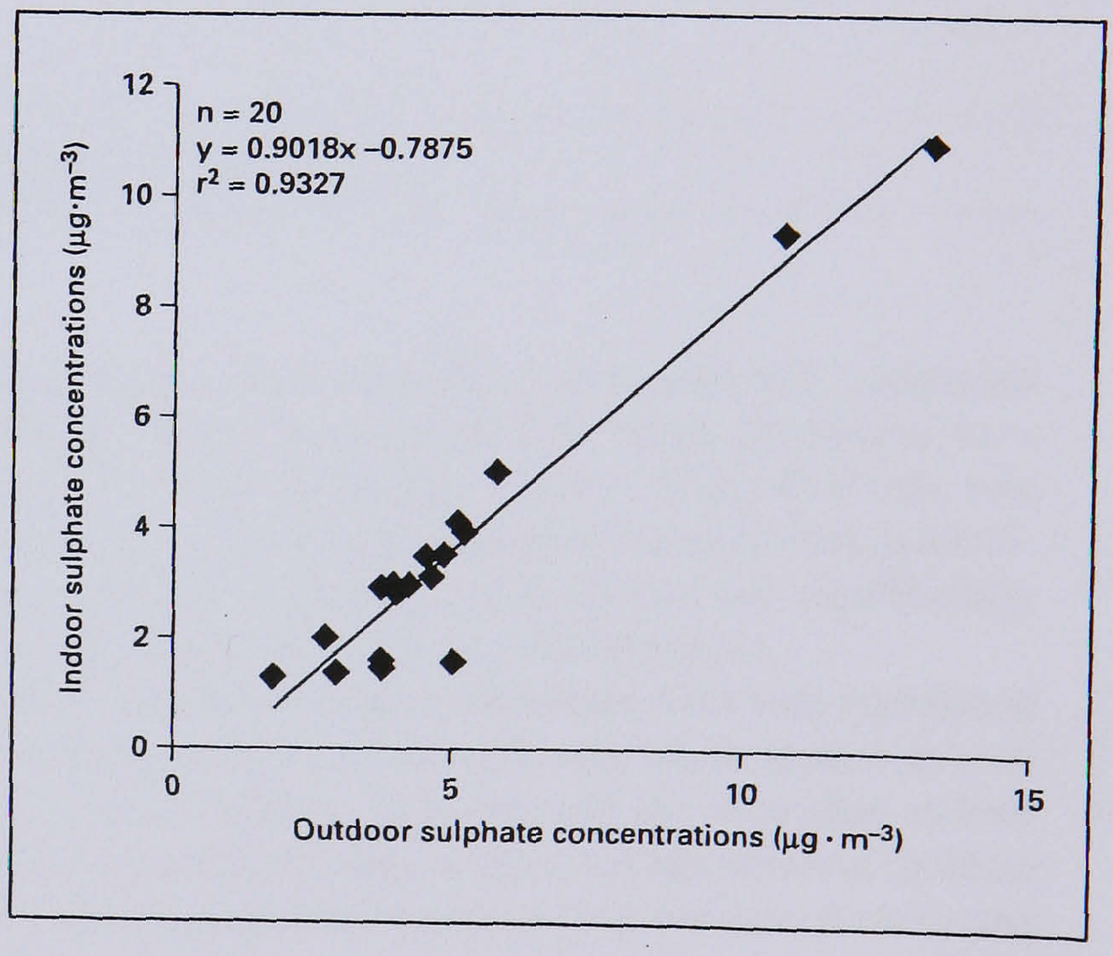


Fig. 9. Regression analysis of outdoor sulphate concentrations and indoor sulphate concentrations.

Table 1. Mean concentrations and mean I/O ratios for elements and anions in indoor and outdoor respirable particulate matter

	Indoor		Outdoor		I/O ratio	
	mean concentration	SE	mean concentration	SE	mean	SE
Zn, $ng \cdot m^{-3}$	179.50	8.51	242.1	6.97	0.69	0.04
Cu, $ng \cdot m^{-3}$	24.99	1.71	43.3	1.51	0.56	0.04
Mn, $ng \cdot m^{-3}$	4.18	0.55	15.6	1.38	0.29	0.03
Al, $ng \cdot m^{-3}$	52.90	4.05	305.2	13.9	0.18	0.01
Sulphate, $\mu g \cdot m^{-3}$	3.47	0.57	4.72	0.61	0.71	0.03
Nitrate, $\mu g \cdot m^{-3}$	0.35	0.06	1.08	0.11	0.37	0.05
Chloride, $\mu g \cdot m^{-3}$	0.15	0.02	1.08	0.18	0.11	0.02

Table 2. Correlation coefficients for metal concentrations in indoor and outdoor particulate matter[1]

	Indoor				Outdoor			
	Zn	Cu	Mn	Al	Zn	Cu	Mn	Al
Indoor								
Zn	–	–	–	–	0.459	–	–	–
Cu	–	–	–	–	0.366	0.615	–	–
Mn	–	–	–	–	–	–	–	–
Al	–	–	–	–	–	–	–	–
Outdoor								
Zn	–	–	–	–	–	0.742	–	–
Cu	–	–	–	–	–	–	–	–
Mn	–	–	–	–	–	–	–	0.551
Al	–	–	–	–	–	–	–	–

[1] Only those coefficients where $p < 0.1$ are quoted.

Conclusion

Although the masses of indoor respirable particulates were lower than those from outdoors there was some degree of correlation between concentrations measured inside the building and outdoor concentrations. This finding suggests that indoor particulate concentrations were driven by ambient concentrations. It was also observed that meteorological factors that lead to a decrease or increase in ambient concentrations were reflected in a subsequent decrease or increase in indoor concentrations. This also suggests that outdoor concentrations are the driving force behind indoor concentrations for this building. Wind speed was found to be important for the quantity of outdoor particulate penetrating indoors, possibly due to the presence of pressure gradients between indoors and outdoors. However, wind speed seemed to have no relationship with particulate concentrations measured outdoors, likely to be because of close proximity to a strong source of particulate matter. Wind direction was the most important meteorological factor for the penetration of outdoor particulates indoors and also significantly affected indoor and outdoor concentrations.

Personal exposure concentrations were well correlated with indoor concentrations although less so than with outdoor concentrations. This supports the view that indoor monitoring of particulate levels is a more efficient method of estimating personal exposure than outdoor monitoring alone.

It seems possible that Zn and Cu may be useful elements for the tracing of vehicle particulate emissions, but only in regions where other sources of the elements are largely absent. It is also clear that Zn, Cu and sulphate appear to be associated mainly with fine particulate matter.

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THE CHARACTERISATION OF SETTLED DUST BY SCANNING ELECTRON MICROSCOPY AND ENERGY DISPERSIVE X-RAY ANALYSIS

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Abstract. Settled dust has been collected inside the main foyers of three University buildings in Wolverhampton City Centre, U.K. Two of the three buildings are located in a street canyon used almost exclusively by heavy duty diesel vehicles. The dust was collected on adhesive carbon spectro-tabs to be in a form suitable for analysis by scanning electron microscope and energy dispersive X-ray analysis. Using these analytical techniques, individual particle analysis was undertaken for morphology and chemistry. Seasonal variations and variations due to location were observed in both the morphological measurements and chemical analysis. Many of the differences appear attributable to the influence of road traffic, in particular, the heavy duty diesel vehicles, travelling along the street canyon.

Keywords: airborne particulate matter, diesel emissions, dust soiling, indoor dust, scanning electron microscope, settled dust

1. Introduction

Air pollution caused by road traffic is an important factor when considering the appraisal of road schemes. This appraisal currently focuses on the road side concentrations of traffic related pollutants, which are potentially harmful to human health or ecological systems. However, particulate vehicle emissions, especially from heavy duty diesel engines, can cause nuisance problems, including the soiling of buildings through the accumulation of dust (QUARG, 1996) and, may also, be partly responsible for sick building syndrome (Gyntelburg *et al.*, 1994). The soiling of buildings on the outside due to traffic emissions is a well known occurrence (Smith and Warke, 1995). However, inside a building, in close proximity to a busy road, the rate of dust soiling and the composition of the settled dust has not received as much attention, although papers have been published in related areas (Brooks and Schwar, 1987; Ford and Adams, 1999; Raza *et al.*, 1990; Williams and McCrae, 1995). In terms of the nuisance that dust soiling causes indoors, factors such as the colour of the dust and the surface upon which the dust settles are likely to be important. As dust produced by traffic emissions tends to be darkly coloured and surfaces in commercial buildings are often light in colour, it may be assumed that

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relatively low levels of traffic derived dust can produce a serious soiling problem inside commercial buildings.

This article introduces a method which can be used for the collection of settled dust in a form suitable for physical and chemical analysis by Scanning Electron Microscope (SEM) and Energy Dispersive X-ray Analysis (EDX). Using this method the settled dust has been characterised chemically and morphologically. Three buildings have been used to investigate the variations in the chemistry and morphology of settled dust dependent upon location. In addition, seasonal variations have also been examined.

2. Materials and Methods

Settled dust was collected inside the main foyers of three University buildings located in the centre of Wolverhampton, U.K., and analysed by SEM (Camscan SV2) and EDX (Link Analytical). Dust soiling rates were also determined for each location, using a gravimetric method. All monitoring was carried out on a monthly basis for one year between November 1999 and October 2000. Exposure periods were for one calendar month beginning on the 15th of each month, for example, the exposure for the month of November would be between 15 November and 14 December.

The foyers are located at ground level and are similar in terms of size and the degree of usage by students and staff. Buildings 1 and 2 are located on either side of the main approach road to the city's primary bus station. This road is, therefore, used by several thousand heavy duty diesel buses each day. The road is closed to other vehicles, so the buses contribute almost 100% of the traffic using the road. Traffic is held up at traffic lights at one end of the road regularly causing queues of vehicles idling outside the two buildings. Four and five storey buildings on both sides of the road produce a small street canyon effect which may impede the dispersion of traffic related emissions. Previous work has demonstrated that high concentrations of airborne particulate matter exist both inside and immediately outside these two buildings (Giess, 1998). Building 3 is located approximately 300 m away from the other two buildings in a different road and is not within a street canyon. This road is only occasionally used by heavy duty diesel vehicles and does not carry high traffic flows.

The measurement of dust soiling rates was achieved by using 5 pre-weighed glass microscope slides coated in a thin, even layer of grease (petroleum jelly) to prevent the removal of dust from the slide during collection, transport and subsequent weighing. To ensure an even layer of grease the slide was gently heated until the grease had melted evenly over the slide surface. Post-weighing of the slides enabled the determination of dust soiling rates in mg m^{-2} day^{-1}. Control slides left in dust free enclosures open to the air demonstrated that there was no significant weight loss due to evaporation or drying of the grease, with this loss

being less than 0.1 mg for a period of one month. Slides spiked with a known quantity of dust showed that there was no measurable loss of dust during transport of the slides. Therefore, any error in the gravimetric measurements can be assumed to be less then ±0.1 mg, being less than 5% of a typical dust loading of 2 to 3.5 mg. All weighing of glass slides was performed on a Mettler Toledo micro-balance with a readability of 0.1 mg. The locations of the slides inside the building foyers were away from radiators and air conditioning outlets/inlets. Cleaning staff were also instructed not to interfere with the slides. The cleaning regime is the same for each of the buildings and does not alter throughout the year. Therefore, the exposure environments of the slides from building to building was almost identical.

Settled dust for SEM and EDX analysis was collected on carbon SEM stubs with carbon low contaminant spectro-tabs attached (Supplied by Agar Scientific, Stansted, U.K.). The spectro-tabs are weakly adhesive on both sides hence they easily attach to the stubs and once dust particles settle, they adhere to the surface of the tab. Each stub was left in the appropriate location at approximately 1.5 m above ground for a month to enable the collection of sufficient dust for analysis. The stubs and slides were placed in locations where they were not interfered with by students and staff using the buildings.

Using SEM measurements of particle size, aspect ratio and chemistry (determined semi-quantitatively by EDX) were made of particles on each stub.

For individual particle analysis, all particles were randomly selected. Particle size and aspect ratio was measured by obtaining an image of 202 individual particles from each stub. Image analysis software (Scion Image) was then used to measure the particles and to determine aspect ratio. For 100 of these particles elemental content was determined semi-quantitatively by EDX. The Link Analytical EDX used for this analysis is capable of analysing for all elements with an atomic mass greater than neon.

3. Results and Discussion

It is not possible to directly relate the dust soiling rates published in other papers with the values measured here due to the wide range of methods used. However, other researchers have obtained comparable results of between 22 and 37 mg m^{-2} day^{-1} (Rufus *et al.*, 1998). For the month of April in Building 3 there is a high peak in the dust soiling rate. Although there was a small amount of construction work being carried out in the vicinity of this building, it is unlikely that this was the cause of this peak. A possible explanation is contamination of the slides during the exposure period leading to an artificial increase in the mass of dust collected. However, no obvious contamination mechanism was observed during the study. Dust soiling rates for the three buildings show no noticeable seasonal variation, with soiling rates for Building 3 being fairly constant after the removal of the

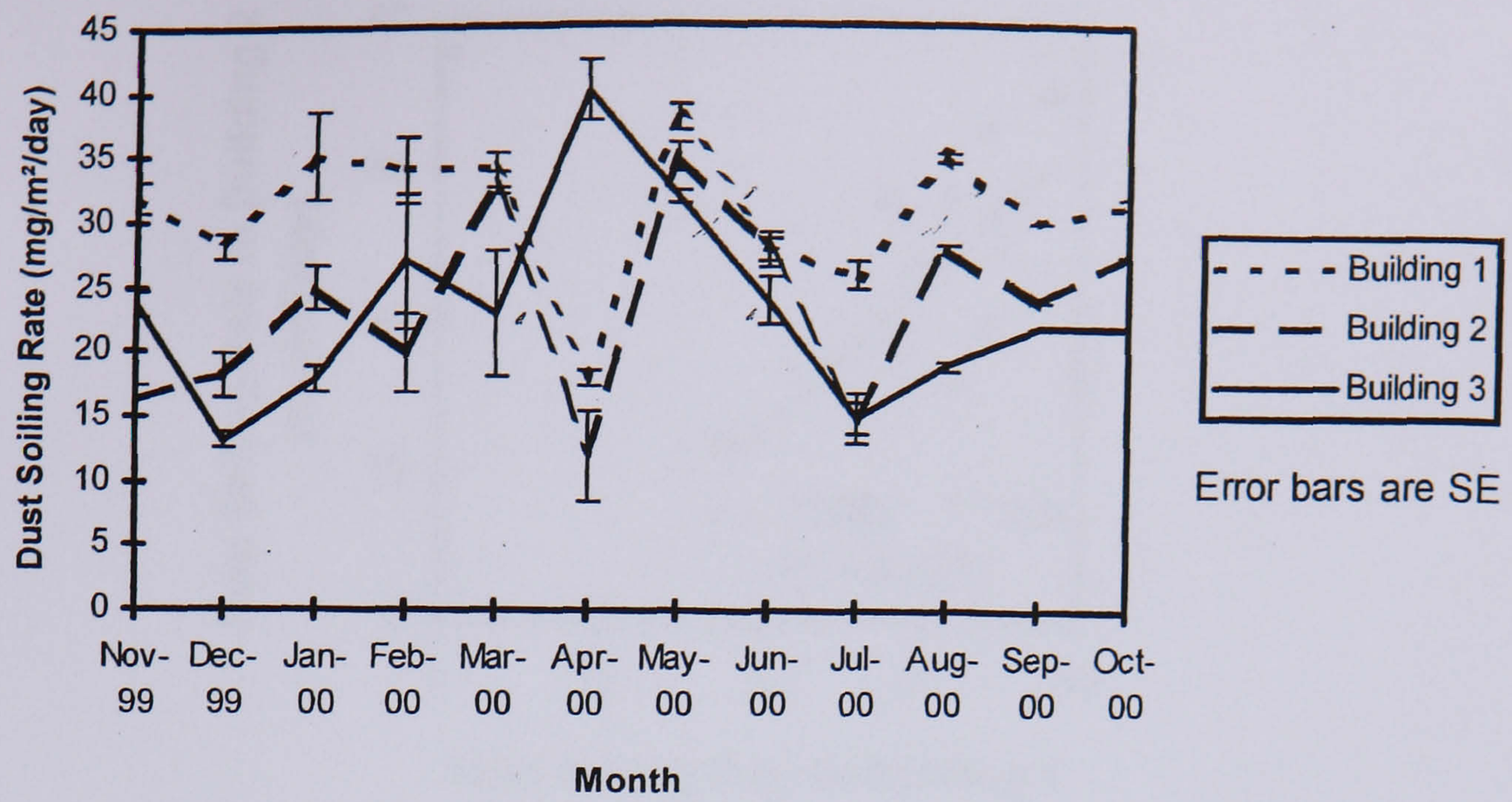

Figure 1. Variation in dust soiling rate for the three sampled buildings in the centre of Wolverhampton.

anomalous result for April (Figure 1). The soiling rates for Buildings 1 and 2 are more variable, but also follow no obvious seasonal trend.

Bate and Coppin (1990) have suggested a threshold limit of 200 mg m^{-2} day^{-1} for dust soiling to be considered a severe nuisance. While other literature propose threshold limits varying from 133 to 350 mg m^{-2} day^{-1}. When compared to these suggested thresholds the soiling rates measured in these buildings can be considered as relatively low. Results show that the foyer in Building 1 has a higher average dust soiling rate than the other two buildings. ANOVA analysis of the three sets of data indicate that this difference is statistically significant ($p < 0.05$, n = 12). After removal of the anomalous results for April this difference is still statistically significant ($p < 0.05$, n = 12). A likely explanation for the elevated dust soiling rates in Building 1 is due to the main door to this building being almost in constant use and also being poorly fitted leaving visible gaps around the door when closed. This allows air from outside to easily penetrate the building shell. When the building is not in use particulate matter can then continue to settle on surfaces inside the building. In contrast Building 2, which is located on the opposite side of the road, has a double door system which appears to offer a more efficient barrier to ambient particulates, therefore, reducing the rate of dust soiling inside the foyer. A paired *t*-test comparing the dust soiling rates inside Building 2 to the dust soiling rate inside Building 3, indicates no significant difference between the two sets of data, further suggesting the effectiveness of the double door system of Building 2 filtering out ambient particles generated within the street canyon.

However, although soiling rates are consistently greater in Building 1 than in Building 2, the soiling rates inside Buildings 1 and 2 are well correlated with a similar trend over time. This may indicate that the dust settling inside these two

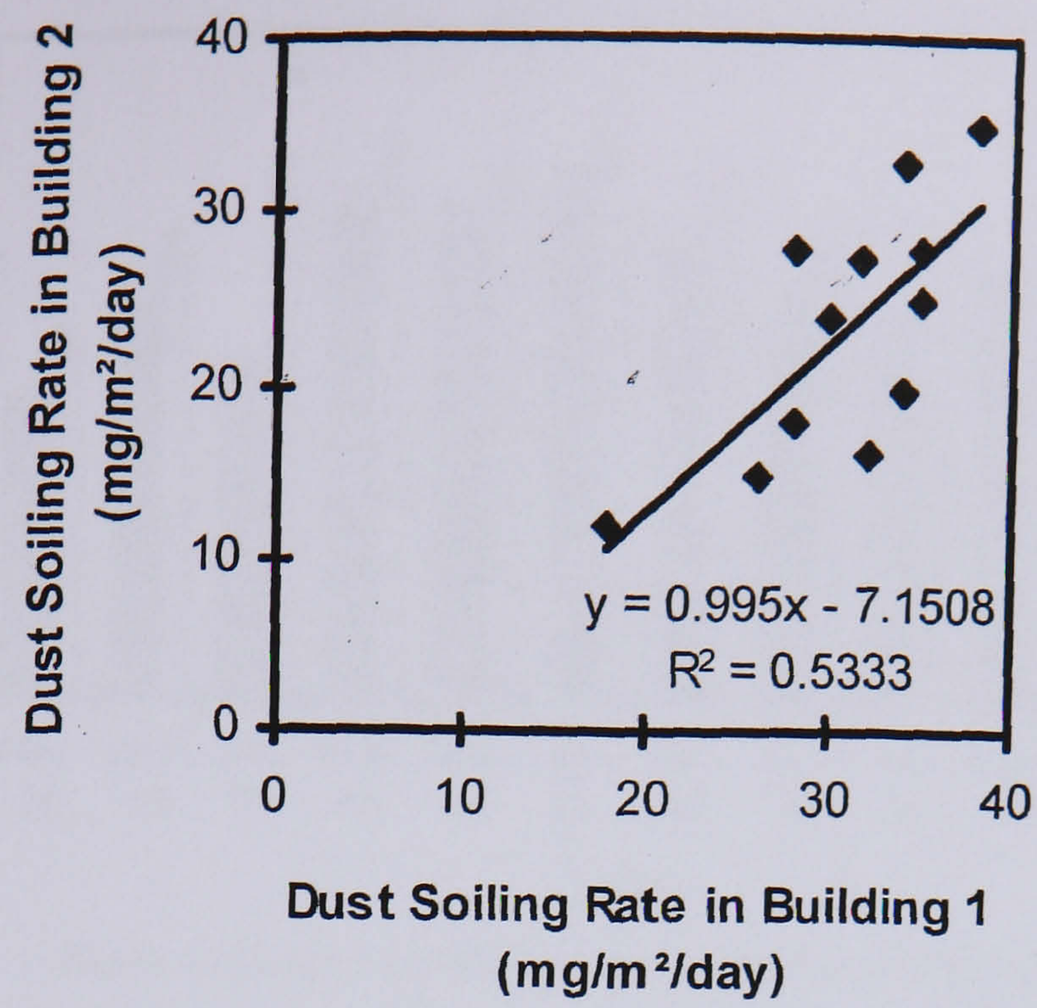

Figure 2. Regression analysis of dust soiling rate (mg m^{-2} day^{-1}) in Building 1 compared with dust soiling rate in Building 2.

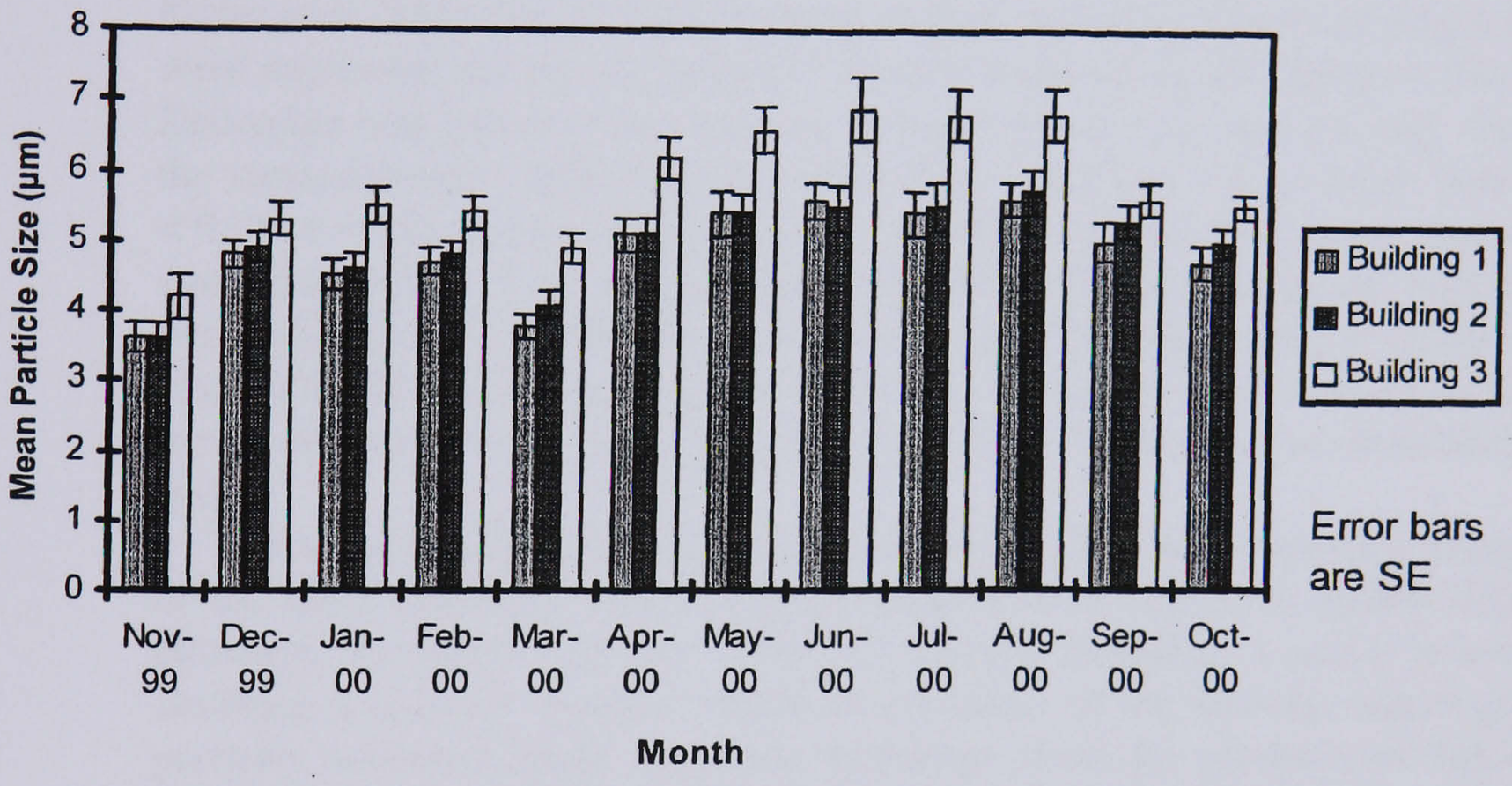

Figure 3. Monthly variation in mean particle size of settled dust in all three buildings.

buildings is from similar sources, likely to be re-suspended road dust and diesel exhaust particulate. A regression analysis of the dust soiling rates inside Building 1 against dust soiling rates inside Building 2 further illustrates this relationship (Figure 2), giving an R^2 value of 0.533 and with the removal of the anomalous results for April this correlation increases to 0.623 ($p < 0.02$, n = 12), showing a significant correlation.

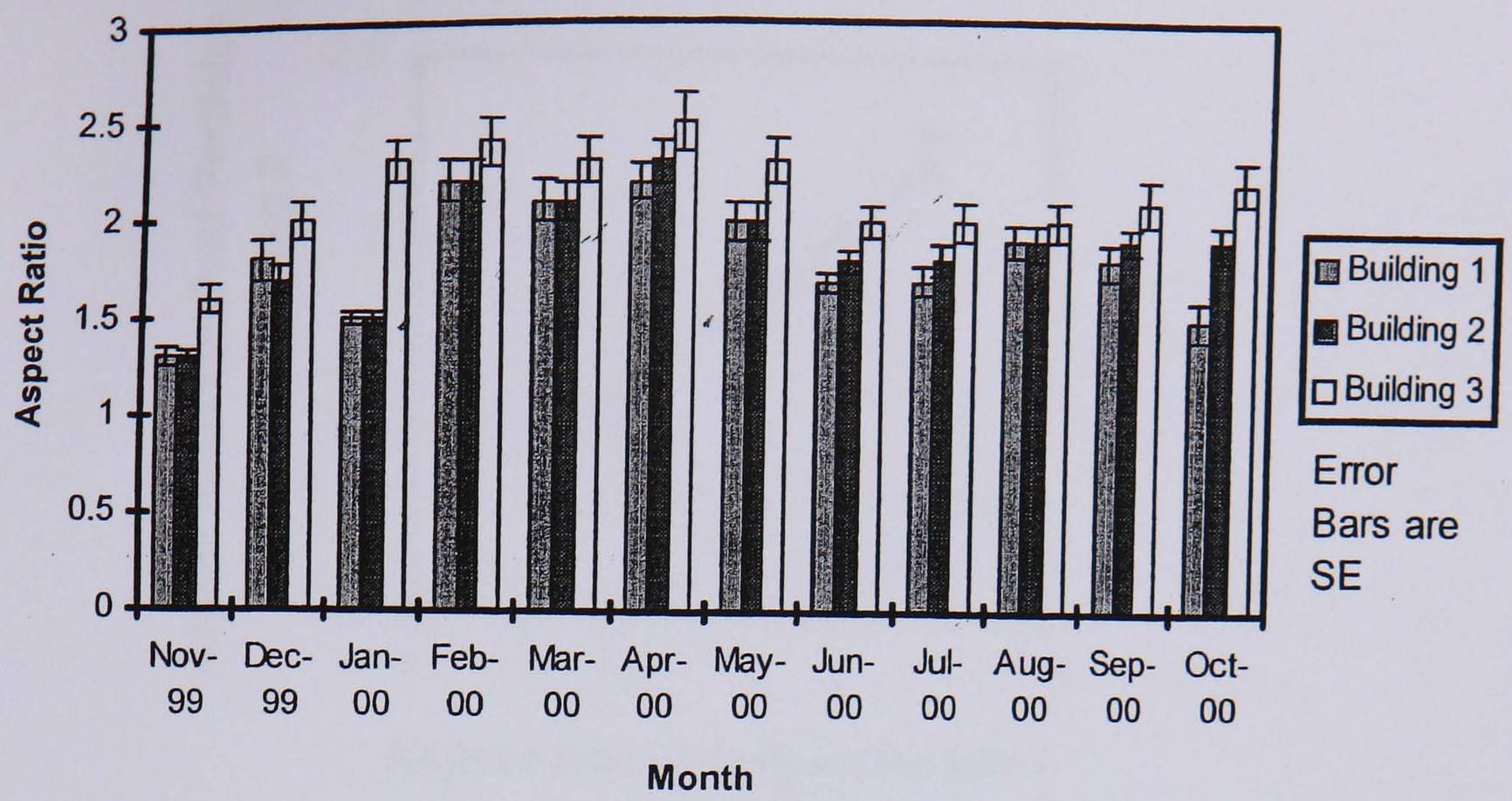

Figure 4. Monthly variation in aspect ratio for all three sampled buildings.

Settled dust particle size shows a seasonal variation with the average particle size being larger during the summer months than the winter months (Figure 3). Rufus *et al.* (1998) in a study of deposited dusts in houses found that larger particles were deposited during the summer. A *t*-test between winter samples (November, December and January) and summer samples (June, July and August) shows that the summer/winter difference is statistically significant for all three buildings ($p < 0.05$, $n = 12$). These larger particles possibly originate from wind blown soil or street dust, which were not re-suspended during the damper winter period. In the two buildings located adjacent to the bus route, for every sample the particle size is smaller than for the corresponding Building 3 samples. This is likely to be due to the presence of smaller diesel exhaust particles present in samples from Buildings 1 and 2.

The aspect ratio of the settled dust shows no discernible seasonal trend in any of the three buildings and is highly variable from month to month (Figure 4). However, the aspect ratio for settled dust inside Buildings 1 and 2 is lower than Building 3 in every sample. Visual examination of the electron micro-graphs of particles collected inside these two buildings show the presence of sub-micron, spherical particles (Plates 1 and 2). Particles of this type tend to be produced by combustion processes, with the only form of combustion in the local vicinity being the traffic on the adjacent road. Occasional agglomerations of very small particles were also observed inside Buildings 1 and 2 (Plate 3). Diesel particles often occur in this form (Berube *et al.*, 1999), hence this may indicate the presence of diesel particle contamination. Both the small spherical particles and the agglomerations were absent in the Building 3 samples. Regression analysis between the aspect ratio of particles inside Building 1 with the aspect ratio of particles inside Building 2 shows a very strong correlation between the two samples (Figure 5), giving an R^2

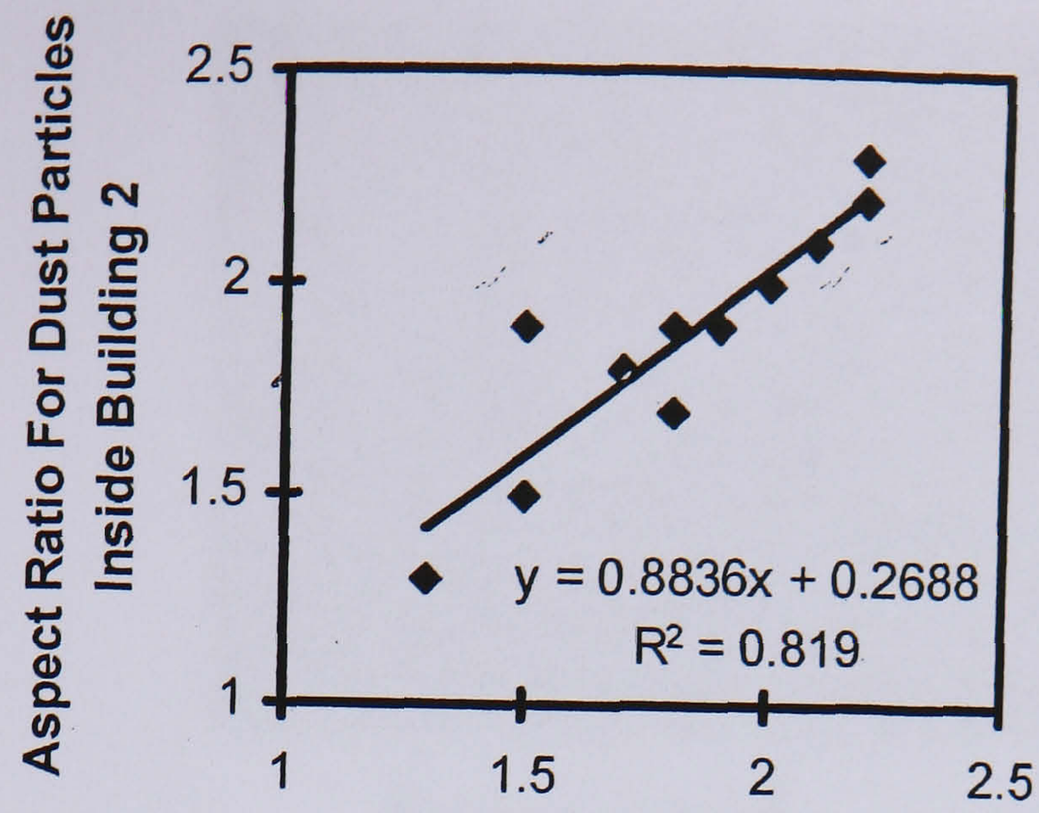

Figure 5. Regression analysis between the aspect ratio of Building 1 and the aspect ratio of Building 2.

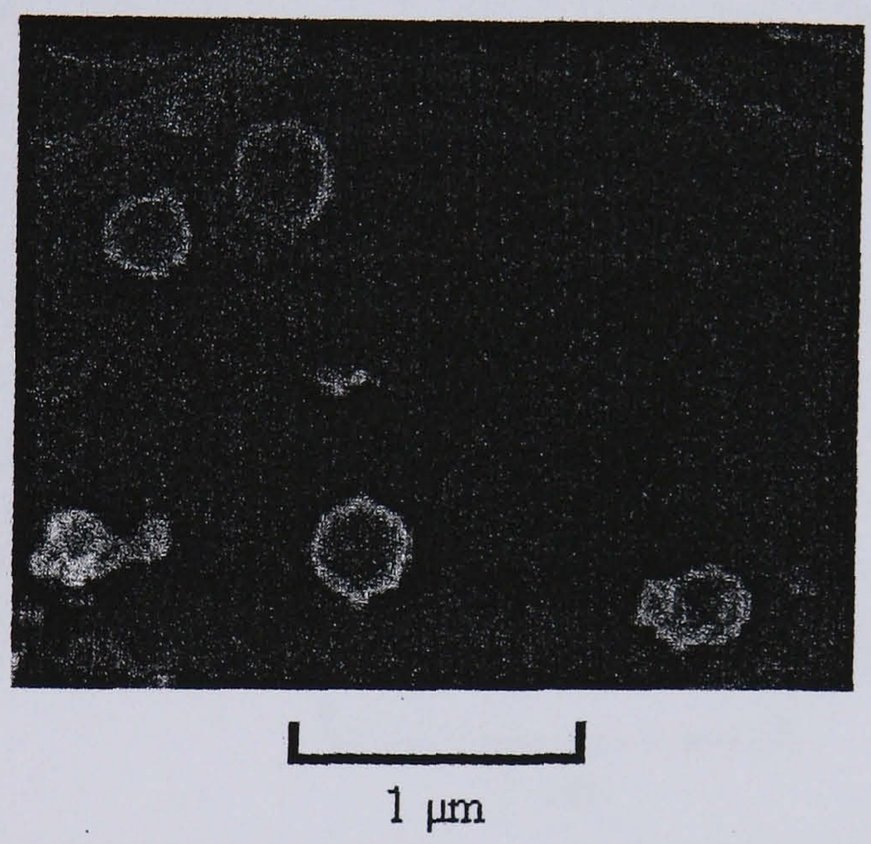

Plate 1. Electron micro-graph of settled dust particles collected in Building 1.

value of 0.819 ($p < 0.001$, n = 12). This may also be indicating that the particles inside the two buildings originate from the same sources.

The influence of traffic related particulate matter on the indoor settled dust is clearly shown by the EDX analysis. The percentage of Na and Cl rich particles (defined as particles containing greater than 70% Na and Cl) present in the settled dust is highly dependent upon season (Figure 6). The percentage of Na and Cl rich particles present in the samples is far greater during the winter than the summer, with these particles likely to be originating from re-suspended rock salt applied

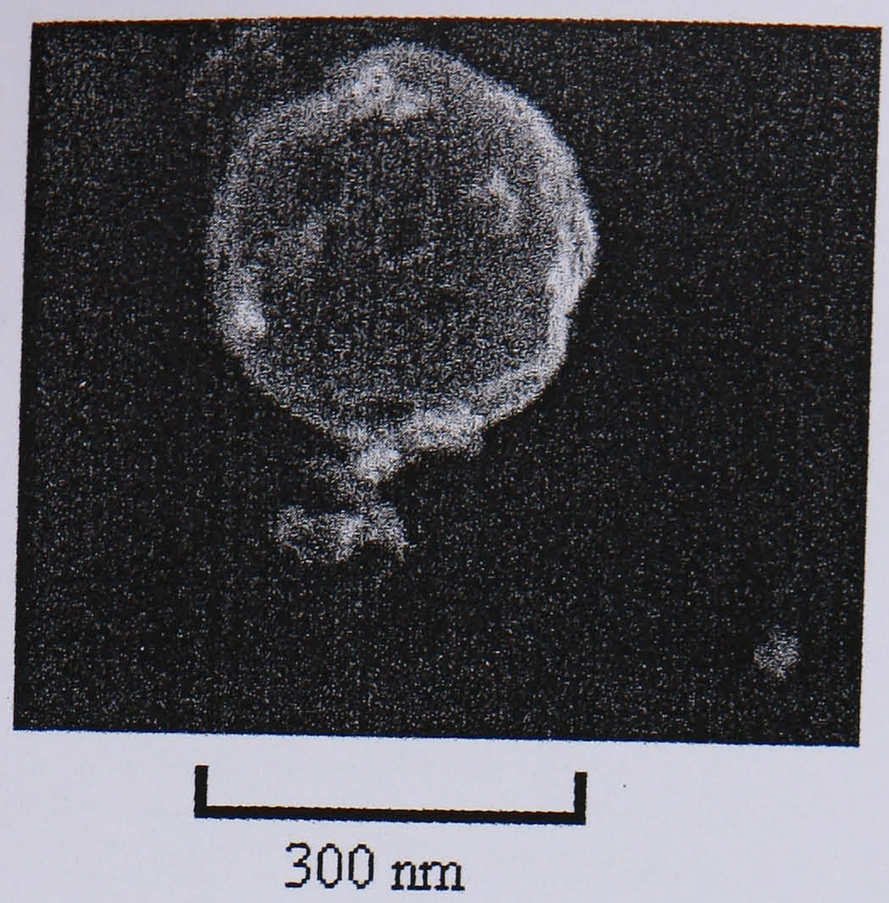

Plate 2. Electron micro-graph of individual settled dust particle collected in Building 1.

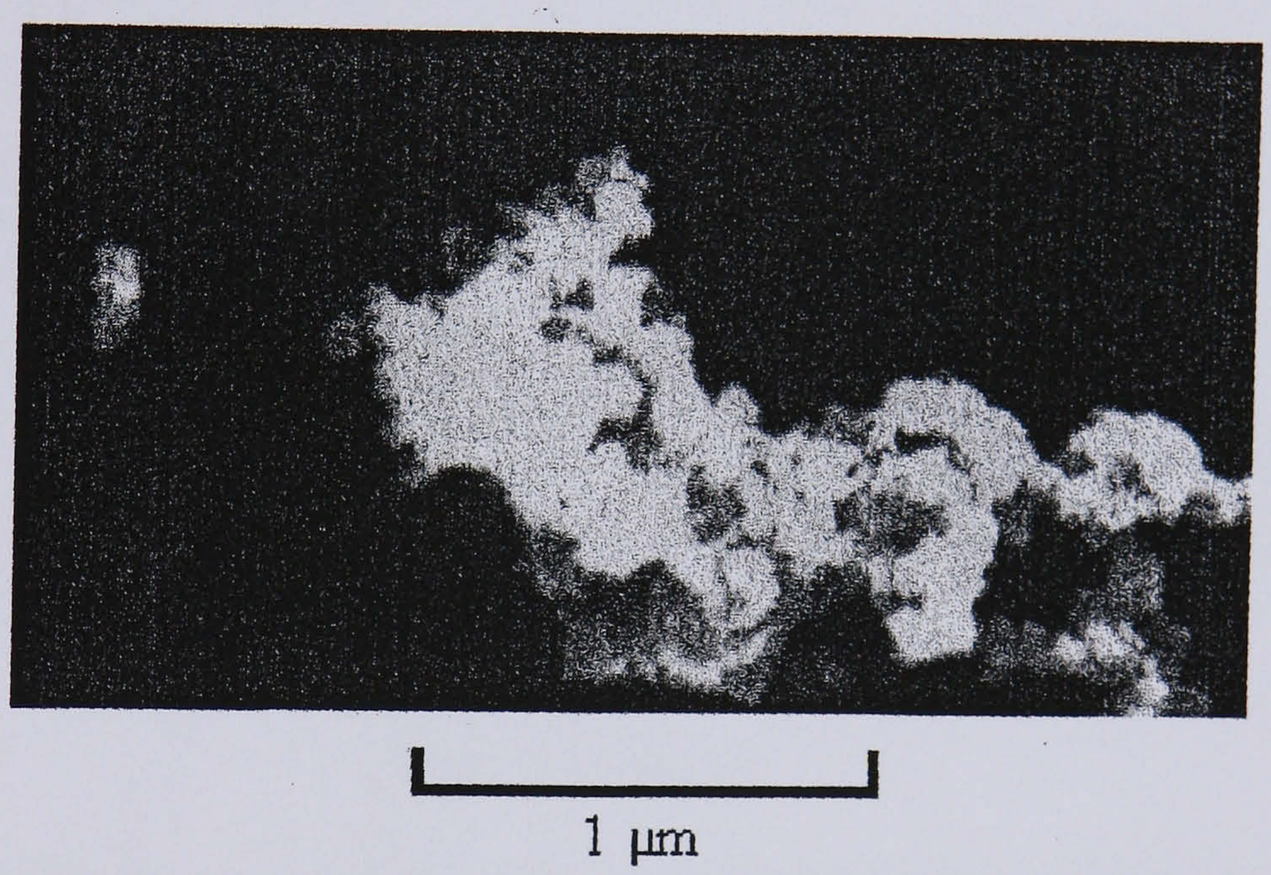

Plate 3. Electron micro-graph of particle agglomeration inside Building 2.

to roads as a de-icing agent. The results also show that Na and Cl rich settled dust particles are present in equal amounts for all particle sizes, suggesting that re-suspended road dust can contribute a range of particle sizes to airborne particulate matter. It is worth noting that marine contributions to the presence of sodium and chlorine rich particles in these buildings is likely to be lower than in other U.K. cities as Wolverhampton is located approximately 125 km away from the nearest coastline.

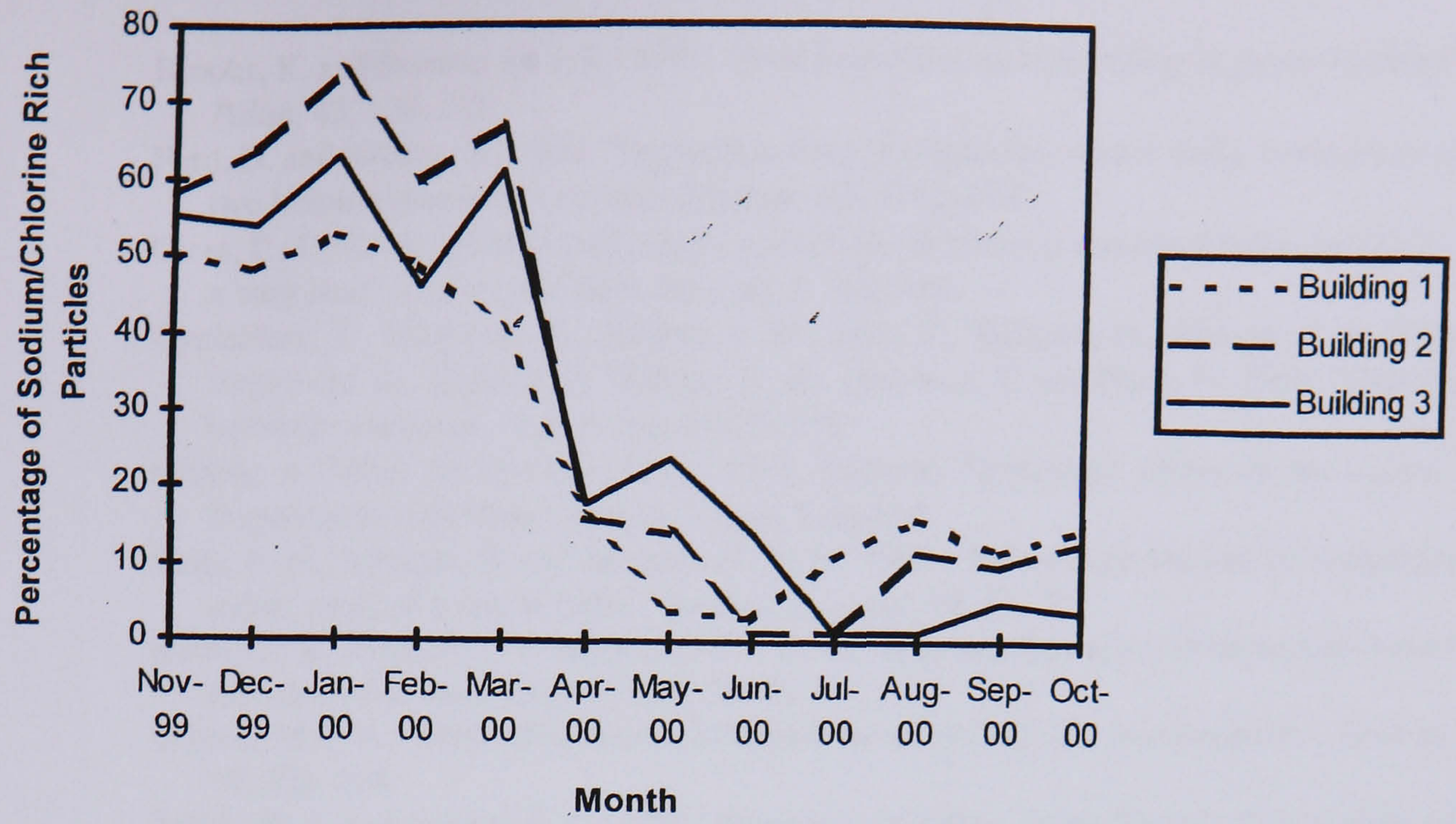

Figure 6. Monthly variation in the percentage of sodium and chlorine rich particles in each building.

4. Conclusion

The results presented here indicate that the proximity of a building to a busy road can affect both the chemical and physical characteristics of indoor settled dust, but may not affect the rate of dust soiling in terms of mg m^{-2} day^{-1}. Other factors may be of more importance, such as air exchange rate and building use.

Even though an increase in particle size was found during the summer months, there was not an associated increase in the dust soiling rate, as would be expected. This is likely to be because the increase of particle size did not cause a sufficient increase in mass to be detectable by the balance.

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